TIGHT BINDING BOOK

CHEMICAL COMPOSITION

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AN ACCOUNT OF THE METHODS BY WHICH ATOMIC WEIGHTS AND MOLECULAR FORMULÆ HAVE BEEN DETERMINED

BY

A. K. GOARD, M.A., Ph.D.

LATE SENIOR SCHOLAR OF TRINITY COLLEGE, CAMBRIDGE; AND HEAD OF THE SCIENCE DEPARTMENT, MARLBOROUGH COLLEGE

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"It is always safe and philosophic to distinguish, as much as is in our power, fact from theory; the experience of past ages is sufficient to show us the wisdom of such a course . . . I cannot doubt but that he who, as a wise philosopher, has most power of penetrating the secrets of Nature, and guessing by hypothesis at her mode of working, will also be most careful, for his own safe progress and that of others, to distinguish that knowledge which consists of assumption . . . from that which is the knowledge of facts and laws; never raising the former to the dignity or authority of the latter, nor confusing the latter more than is inevitable with the former."—FARADAY, *Experimental Researches in Electricity*, Vol. II, 1844, p. 285.

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PREFACE

This book attempts to set out the evidence which we possess concerning atomic and molecular weights (excluding "abnormalities" due to association and dissociation of molecules) in a way which shall enable the reader to view the whole subject in perspective. Within its limits, it is hoped that the account is fairly complete.

The basis of the treatment is frankly theoretical; though a number of experimental methods are described, it is not intended that such descriptions should take the place of first-hand knowledge; no descriptions, however lucid, can do this. Again, it is assumed that the reader has already some elementary knowledge of chemistry, and has access to the usual text-books.

In order that Dalton's theory should be properly appreciated, it is necessary to have some idea of the general state of chemistry at the time when the theory was first put forward. For this reason, the earlier chapters deal in outline with those portions of chemical history which are relevant to the subject. Some feel a faint resentment at being asked to approach a science in this way; they ask why they should trouble themselves about old theories now outworn. There is certainly much in the early history of chemistry which only concerns the specialist; but this can hardly be said of the growth of atomic and molecular theories, in which we can trace in the most interesting way the development and application of the principles by which scientific knowledge is won. The author, at least, can vouch for the fact that this part of the subject becomes more, and not less, engrossing the further it is studied.

The writer acknowledges his indebtedness to many

sources, chief among which (apart from original papers) have been Ida Freund's *The Study of Chemical Composition*, Whewell's *History of the Inductive Sciences*, and those portions of Ostwald's *Lehrbuch der Allgemeinen Chemie* which deal with the properties of dilute solutions. His thanks are also due to the Alembic Club, for kind permission to reproduce certain statistics from Cannizzaro's *Sketch of a Course of Chemical Philosophy*.

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A. K. GOARD.

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PART I

THE EARLY HISTORY OF CHEMISTRY

CHAPTER I

ON DIFFERENT MODES OF REASONING

"Scientific astronomy, as distinguished from mere star-gazing, can hardly claim an age of more than 3,000 years. It is less than this since Pythagoras, Aristarchus and others explained that the earth moved round a fixed sun. Yet the really significant figure for our present purpose is not so much the time since men began to make conjectures about the structure of the universe, as the time since they began to unravel its true structure by the help of ascertained fact. The important length of time is . . . a mere three centuries or so."—SIR JAMES JEANS, *The Universe Around Us*.

CHEMISTRY may claim in one sense an antiquity at least equal to that of astronomy. Dr. Holmyard says that "to discover the origin of chemistry takes us back some 5,000 or 6,000 years to the early days of ancient Egypt"; that is, to the days in which the Egyptians practised the extraction of metals, the manufacture of glass, soap, and so forth. Again, theoretical chemistry may be said to begin with the earliest speculations upon the constitution of matter; speculations which began at least as early as the fifth century B.C. On the other hand, regarded from the modern scientific standpoint, little real advance was made in systematic and theoretical

chemistry until about the middle of the seventeenth century A.D. The history of chemistry, therefore, is similar to that of astronomy, and indeed of all other sciences, in that a prodigious change in its rate of progress began about 300 years ago.

In order to understand the reasons for this change, it is necessary to consider briefly the modes of reasoning which lie at the root of attempts which have been, and are being made, to find out the truth about the Universe in which we live.

One of the earliest processes of thought, and the first to be clearly expounded, is that of *deduction*. In reasoning by deduction, we start with a statement of a general nature; some law, or axiom, the truth of which must be taken for granted; and from this, it is shown that some particular statement must be true. A good example of deductive reasoning is a theorem of Euclid. At the beginning of his geometry, Euclid lays down certain axioms; if we accept these, the particular conclusions which he draws follow inevitably.

For example, in proving the theorem which states that "The angles at the base of an isoceles triangle are equal," it is quite unnecessary to draw an isosceles triangle, and to measure the angles at its base, in order to be satisfied of the truth of the theorem. The equality of the angles follows logically from the propositions which Euclid lays down as the foundations of his geometry. Most mathematical reasoning is of this kind, namely, drawing logical conclusions from certain statements which are assumed to be true for the purposes of the process.

The foundation of deductive reasoning is the syllogism, which was developed and clearly formulated by Aristotle (384–322 B.C.). The simple syllogism consists of three stages:

The MAJOR PREMISE: a general statement applying to some class of objects;

The MINOR PREMISE: a more limited statement containing some reference to an object included in the major premise;

CONCLUSION: a statement referring to this object; and the inevitable consequence of the truths contained in the major and minor premises.

This is best shown by taking an example:

> MAJOR PREMISE: All metals conduct electricity.
> MINOR PREMISE: This substance is a metal.
> CONCLUSION: Therefore this substance conducts electricity.

If the two premises are true, the conclusion must also be true. There are, however, two possibilities of error in the use of a syllogism:

(*a*) The reasoning may be faulty. For example, in the following syllogism:

> MAJOR PREMISE: All metallic oxides are solids.
> MINOR PREMISE: This substance is a solid.
> CONCLUSION: Therefore this substance is a metallic oxide.

The conclusion is not necessarily correct, because other substances besides metallic oxides are solids.

(*b*) The premises may not be true, as in the following syllogism:

> MAJOR PREMISE: All metallic chlorides are solids.
> MINOR PREMISE: This substance is a metallic chloride.
> CONCLUSION: Therefore this substance is a solid.

The reasoning is here correct, but the major premise is untrue, as some metallic chlorides are liquids. Hence the conclusion is, or may be, untrue.

These examples illustrate sufficiently the chief features of deduction. Though it is a useful, even an essential,

part of the process of finding out the truth about things, it has its limitations. Even if we reason correctly, according to the " rules of logic," we may still be wrong in our conclusions, because our premises may be wrong. In these days of modern science, we have learnt to be cautious in accepting as true a number of statements which appear—and which have appeared in the past—as " axiomatic," or " self-evident." Euclid's axioms, for example, are no longer held to be necessarily true of *real* space, although they appear to most of us to be so obviously true as to need no proof.* This does not mean that Euclid's theorems are " untrue " ; if his axioms are accepted, as rules of the game, so to speak, his conclusions are unassailable ; they are true of " Euclidean space," *i.e.* space according to the rules of Euclid. Nature, however, does not seem to agree with Euclid. To pursue this any further would take us out of our depth ; but remember that deduction, while enabling us to draw inevitable conclusions from certain statements accepted as true, does not concern itself *essentially* with the truth or untruth of these initial statements.

Science uses deduction, but only as a tool. The main task of the scientist is the opposite of deduction ; he is faced with a number of experimental facts, and has to try to discover laws which connect these facts. Deduction, as we have said, argues from the general to the particular ; science usually has to proceed from the particular to the general ; and to do this it makes use of the process known as *induction.*

A simple induction consists of three main steps.

(1) The collection of the *relevant* facts. (This is often a difficult task ; it may require a great genius to select the really important facts, and to reject those which have little or no bearing upon the matter in hand. The work of the scientist is here similar to that of the detective

* *E.g.* the statement that " a straight line is the shortest distance between two points."

searching for " clues " ; not all men are equally quick to seize upon important clues, as any reader of detective stories will know.)

(2) Framing a hypothesis which shall explain these facts.

(3) Testing the hypothesis. This is done by *deducing* consequences which should follow logically from the hypothesis, and then seeing, generally by performing an experiment, whether these consequences are actually observed. If the result of the experiment does not agree with the hypothesis, the latter must be modified, or perhaps abandoned altogether.

The peculiar characteristics of modern science are contained in the above. The orderly arrangement, and classification, of " experimental facts," " phenomena," " data," or whatever we like to call them, are the first essential. For successful original work in science acute observation, and a kind of selective instinct which leads the worker on to the right path, are necessary. Some persons are more blessed with these gifts than others ; Faraday was a conspicuous possessor of them. The instinct and the observation may be acquired, however, and in any case developed, by working intelligently—especially by cultivating special powers of observation, and by training the mind to perceive connections between different sets of phenomena.

Again, imagination in framing hypotheses is required. Here we may emphasise that if the hypothesis is to be of any value scientifically, it must be capable of experimental verification ; otherwise it remains a mere speculation, which may or may not be true. Evidently, to verify a hypothesis we need both logical ability and training in " experimental technique."

It is this resolute testing of hypotheses by experiment which especially distinguishes modern science from ancient. Though the Greeks, for example, had a gift amounting to genius for inventing hypotheses, they

generally neglected or actually despised experiment, with the result that it was often impossible to decide between one plausible theory and another.

Another feature of present-day investigation is the effort, when possible, to examine problems from a quantitative standpoint—that is, to think in terms of *measurement*. It is a remarkable fact that rapid progress in any science has generally dated from the successful application to it of quantitative measurement; we shall see this abundantly illustrated later. At the present day, this habit of "thinking quantitatively" is almost second nature with most research chemists and physicists, and forms a striking contrast to the attitude, for example, of the alchemists, who were chiefly concerned with describing the *qualities* of different substances.

"Facts," "Laws," and "Theories"

The beginner who wishes to think clearly should draw a sharp distinction in his mind between the above. Consider, for example, such statements as the following:

(1) Caustic soda solution, added to copper sulphate solution, produces a blue gelatinous precipitate.

(2) A given chemical compound always contains the same elements in the same proportions by weight.

(3) Equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.

The first statement is a "fact."

The second is a "law"; that is, it is a generalisation, which is the result of experience. Without elaborating this too much, it may be pointed out that it involves expanding a statement which has been shown to be true in a large number of cases to embrace other cases which have not been yet examined. No exceptions to this particular generalisation have been found in practice; and the more compounds we examine and find to conform to the law, the more certain we become of its universal application.

The third statement is a "theory," or "hypothesis," based on a certain supposition regarding the constitution of matter. This hypothesis, however, leads to so many conclusions which are supported by experiment that we may say that there is very strong indirect evidence of its truth.

To summarise, one should distinguish between *experimental facts* (directly observed, and independent of theories); *laws* (general statements describing the ways in which certain substances, or classes of substances, behave, and also independent of theories); and *hypotheses* or *theories* (suggestions put forward to explain observed facts and laws).

A hypothesis may prove unsatisfactory, and may have to be modified or discarded; but the experimental facts and the experimentally established laws remain, and any new theory which supplants the old must take them into account.

It may be said in conclusion that the "explanations" of science are mainly attempts to connect together different sets of phenomena; that is, to discover laws which shall bind together apparently complex facts into an organised whole. For example, we say that a solution of common salt conducts electricity "because" the sodium chloride splits up into ions of sodium and chlorine; we may go a stage further, and say that the molecule splits up "because" its component atoms are constructed in a certain way; but most scientists are reduced very soon to a confession of ignorance by the simple process of asking "Why?" two or three times in succession. This is not intended to disparage scientific explanation, but to make it clear that science is not generally concerned with what have been called "ultimate" explanations. Scientific men set themselves to examine the constitution of matter, but are usually content to leave on one side the question as to whether matter "really exists." To some persons such questions appear merely academic and of no

practical value whatsoever; to others, they are of absorbing interest. They do not concern us here; the reader who is interested will find the names of a few books dealing with such abstract problems (really the subject-matter of philosophy) at the end of this chapter, though he is warned that some of them are stiff reading!

References

How We Learn (A Short Primer of Scientific Method for Boys), by W. H. S. Jones (Camb. Univ. Press, 1*s*. 6*d*.).

A larger work, which contains valuable summaries of the views of many leading philosophers of different periods, is *Scientific Method*, by F. W. Westaway (Blackie & Son, 15*s*.).

Other books dealing more with purely philosophical problems, are—

The Problems of Philosophy, by Bertrand Russell (Home Univ. Library).

Science and the Modern World, by A. N. Whitehead (and other works by the same author).

Exercises on Chapter I

1. From the knowledge of science which you possess, select six examples each of (*a*) experimental facts; (*b*) scientific laws; (*c*) scientific theories.

2. Discuss the statement "Science is always inventing new theories, and scrapping them after a few years."

3. Select an example, from your scientific knowledge, of each of the following: A generalisation; reasoning by induction; reasoning by deduction; reasoning by analogy.

CHAPTER II

ANCIENT THEORIES CONCERNING THE CONSTITUTION OF MATTER

" Myself when young did eagerly frequent
Doctor and Saint, and heard great Argument
About it and about : but evermore
Came out by the same Door as in I went."

Rubaiyát of OMAR KHAYYÁM.

" The modern atomic doctrine is not by fortuitous coincidence identical with that of Leucippus and Democritus ; but is its direct descendant, flesh of its flesh, and bone of its bone. . . . Democritus is in complete agreement . . . with the actual results of the scientific research of the last three centuries."—GOMPERZ, *Greek Thinkers* (1896).

" The atomic theory of Democritus was a guess, and no more than a guess. Everybody around him was guessing about the origin of things, and they guessed in a great number of ways ; but he happened to make a guess which was more near the right thing than any of the others."—W. H. CLIFFORD, *Lectures and Essays* (1879).

IT is impossible to say when speculation first began as to the nature of matter. Argument about such a point implies a certain amount of leisure ; it is doubtful whether primitive man, largely absorbed in the pressing problems of getting food and of avoiding being eaten himself, worried his head very much about it. An early Indian philosopher, Kanada, concluded that matter was composed of atoms, for the following reason : if matter be capable of infinite division, he argues, any material body

must be composed of an infinite number of particles. If this were so,

> " there would be no difference of magnitude between a mustard seed, a mountain, a gnat and an elephant, each alike containing an infinity of particles."

Now there obviously is a difference of magnitude between these objects ; therefore they cannot contain each alike an infinity of particles, and matter cannot consequently be capable of infinite division. It is an ingenious argument, but a modern mathematician would probably make short work of it.

Kanada lived probably before 1200 B.C. Though other early Indian philosophers speculated to some extent on such matters, nothing approaching Science arose among the Indians themselves, who seem to have lacked anything in the nature of scientific curiosity (*cf.* Sarton's *Introduction to the History of Science*, Vol. 1, p. 69). Some hold that they influenced Greek thought, but this seems very doubtful.

Certainly the Greeks were the first philosophers who may be said to resemble modern European thinkers—though opinions vary as to the extent of the resemblance. They had a most lively curiosity, and immense intellectual energy ; and among other things, set themselves to investigate the nature of the Universe in general, and of matter in particular. The manner in which they did this differs characteristically from the method which would be pursued to-day by a scientific worker ; upon very scanty data they reared vast superstructures, often of perfect logical consistency, but unfortunately often remarkably wide of the truth. They frequently started from some fundamental assumption, the truth of which was taken for granted, and deduced from it consequences which were utterly fantastic. Thus the Eleatics, a school of philosophers flourishing in the fifth century B.C., assumed the absolute unity of all being ; from this they were led

to deny the existence of "void"; and from this, to deny that there is any motion in the Universe. Such a deduction is of course in violent contradiction to the evidence of our senses; but there were not lacking some who preferred to keep their logical systems intact by flatly denying that our senses can tell us anything about the Universe as it really is. It must not be overlooked that a love of logic is in itself a virtue; if a theory is true, it must presumably be logical. The Greeks, however, seemed frequently to assume that if a theory is logical, it must also be true. Aristotle, though critical of the Eleatics on these very grounds, himself demolished the Atomic Theory for reasons substantially as follows: there is no logical impossibility in the idea of dividing anything up into smaller and small particles; into a thousand particles; into ten thousand times ten thousand particles; in his own words, "nothing impossible will have happened, . . . although perhaps no one could perform the division." Hence, matter is capable of infinite division. A modern scientist might retort—"I am not concerned with what may be conceived as possible; I want to find out what actually *is* possible. You say that matter may be divided indefinitely in the imagination; but can it be so divided in practice?" But the Greeks, with their obsession that the truth could be found out by thinking sufficiently hard, were blind to the necessity of verifying their conclusions by the vulgar method of sense testimony. There is an old story of a number of philosophers who were arguing as to how many teeth a horse possesses. After some hours' discussion, one of them ventured to suggest that they should go and see. He was sternly rebuked by the others, who pointed out that by a sufficient application of logical principles the matter could be settled without resorting to such an expedient. The story is a libel, but has the truth of caricature.

We must restrict ourselves, in a short chapter, to

a few of the principal speculations upon the nature of matter, more especially to those which concern the atomic theory.

The Greeks saw that in the world there are many different kinds of matter; different objects have different colours; some are moist, such as water; some hot, such as fire; some heavy, some light, and so on. Nevertheless, they held that all these varying forms of matter were probably derived from a few simple forms, or even from one form; and this was an idea which has continued to dominate scientific thought up to the present day.

If, then, there is only one kind of matter, or at most a few, how can we account for the many forms actually observed? On this point opinion was divided. Anaxagoras (500–427 B.C.) supposed that material things consisted of particles which were of different kinds in different substances; bones were composed of small particles of bone, gold of grains of gold, and so forth. We might regard these particles as analogous to our modern idea of elements. According to Anaxagoras, an individual thing takes its properties from the particles which are present in it in the greatest number; and there are passages in his teaching which suggest vaguely both the idea of compounds, and "a dim glimpse of the idea of chemical analysis" (Whewell, *History of the Inductive Sciences*).

On the other hand, an important school, with which are associated the names of Leucippus, Democritus, (*circ.* 460–360 B.C.) and others, maintained that matter was eternal and indestructible, and was composed of atoms, which were likewise eternal and indestructible (this involving the indivisibility of the atom); but, in opposition to Anaxagoras' theory, they supposed that there was only one kind of matter, the apparently various kinds observed being due to the different shapes and motions of the individual atoms. Hence these philosophers were

able to explain the diversity of things without sacrificing the idea of a single fundamental substance. Their speculations on the nature of atoms are apt to strike the modern reader as somewhat crude ; for example,

" the things which are able to affect the senses pleasantly consist of smooth and round elements ; while all those on the other hand which are found to be bitter and harsh, are held in connection by particles that are more hooked and for this reason are wont to tear open passages into our senses, and in entering to break through the body."

Nevertheless, these philosophers were actually on the right path ; and had they only possessed the spirit of experimental inquiry, there is no knowing how far this theory might have been developed.

Unfortunately perhaps for science, yet another rival view—the doctrine of the four elements—was adopted by Aristotle ; and such was the reverence in which he was held by his contemporaries and by the learned of the Middle Ages, that this erroneous theory held unquestioned sway until the seventeenth century A.D. On account of the extraordinary influence wielded by Aristotle, we must briefly examine his views, as no understanding of early chemistry can be reached without some knowledge of them.

Aristotle (384–322 B.C.) was a pupil of Plato, and lived for much of his life at Athens. His school of philosophy was called the Peripatetic, because, some say, he had the habit of walking about while lecturing. It is impossible in a short space even to enumerate the different branches of knowledge which he undertook to make his own ; and it is especially difficult here to give a just idea of his achievements, because as far as physical science is concerned these achievements fell very far short of their professions. In Aristotle's favour, we may say that he not only clarified the process of deduction by the use of the syllogism (a great work in itself), but that he also

described many of the essential features of the inductive method. In his Metaphysics he says:

> "Science commences when, from a great number of Experiences, one general conception is formed which will embrace all similar cases."

This strongly resembles the description which would be given at the present time of a "Natural Law." Again, in another passage, he remarks:

> "Those who have devoted themselves more to the study of nature are better able to establish principles more widely applicable; though they who start from theories without examining the facts, and take into account only a small number of phenomena, no doubt arrive more easily at their conclusions."

This is a frontal attack; it was the chief failing of the majority of the Greek natural philosophers that they "started from theories without examining the facts, and took into account only a small number of phenomena"; the systems they evolved in consequence could often be maintained only by resolutely ignoring all contradictory evidence, even when this was of the most glaring kind.

Unfortunately, many of Aristotle's criticisms of others could be applied with almost equal force to himself. As we have indicated, he set himself to cover an enormous field; and he had no time in which to verify his theories by experiment. A modern scientist knows that the method of induction, properly applied, is the soundest way of arriving at the truth; but the method is slow, and no one to-day would dare to attempt a tithe of the task which Aristotle imposed upon himself. We may recall the latter's sweeping dismissal of the atomic theory "on logical grounds," which shows that in reality he fell into the same errors as his predecessors; as a further example of his actual methods we may outline the way in which he sought to establish the doctrine of the four elements.

The theory of the four elements was not originated by Aristotle, but he presented it in a way which invested it with plausibility, and made it appear as though it were based upon the strictest logical reasoning.

This reasoning was essentially as follows :

We seek the principles of tangible bodies (*i.e.* those fundamental forms of matter which underlie the various forms actually felt).

Hence we must deal with those qualities only which have reference to the sense of touch.

Such qualities are: hot, cold; wet, dry; hard, soft; heavy, light; unctuous, meagre; rough, smooth; dense, rare.

(For various reasons, all these pairs are rejected, as not being really fundamental, except the first two : hence—)

The four fundamental qualities are hot, cold ; wet, dry.

Four things can be combined in pairs in six ways; but two of these ways must here be rejected as involving a logical contradiction ; a body cannot be hot and cold, or wet and dry, at the same time. Hence the following four pairs remain :

Cold and dry (identified with EARTH).
Cold and wet (identified with WATER).
Hot and dry (identified with FIRE).
Hot and wet (identified with AIR—similar to steam).

These were consequently the four "elements," of which all actual bodies were supposed to be composed. *Actual* earth, water, fire, and air were not considered as identical with the elements, but as containing predominant amounts of one of them. The various forms of matter were thus explained on the supposition that they contained different elements mingled in varying proportions.

It may seem strange to a modern reader that such reasoning should have held the world captive ; but so it did. Aristotle's intellectual eminence, and the logical clarity of his writing, were such that his works later became invested with almost Biblical authority. Thus, Averroës of Cordova (1126–1198) maintained that Aristotle

"carried the sciences to their highest possible degree, measured their whole extent, and fixed their ultimate and permanent boundaries" (Whewell, *loc. cit.*). In the Middle Ages this doctrine of the four elements dominated chemistry, although it underwent certain strange modifications at the hands of the alchemists, of whom we shall say a few words in the next chapter. It was not until the sixteenth century that the revolt began against this domination; but since then many voices have been raised in condemnation of the founder of the Peripatetics.

Aristotle ". . . corrupted Natural Philosophy by his logic, and made the world out of his categories."—Bacon, *Novum Organum*, 1620.

"Aristotle's proceeding from facts, and his inductive mounting from facts to principles, has remained a mere theory, scarcely anywhere put in practice by Aristotle himself. At the most, what he does is to adduce a few isolated facts, and immediately spring from these to the most universal principles, to which he thenceforward dogmatically adheres in purely deductive treatment."—Lange, *History of Materialism*.

"The Aristotelian physics cannot be considered as otherwise than a complete failure."—Whewell, *loc. cit.*

The actual achievements of the Greeks with respect to natural science must then be considered as negligible; very few would seriously maintain, for example, that the resemblance between the atomic theory of Democritus and that theory as it exists to-day is more than slight and superficial. It cannot be too clearly emphasised that there is a very great difference between the Greek method and that of modern science. Greek theories (in spite of the passages quoted from Aristotle) remained for the most part ingenious speculations, which started from a few primary assumptions, and were elaborated with an almost entire disregard of the need for testing each step by experiment; a modern scientific theory, on the other hand, is framed to account for observed facts, and must, if

it is to be accepted, be capable of accounting for those facts, and also to lead to conclusions capable of being verified experimentally ; even then, it will probably have to be modified, or possibly abandoned, as knowledge progresses and fresh facts accumulate.

We shall see this again, still more plainly, in the next few chapters ; but in closing this short survey of Greek materialistic philosophy, it is as well to point out that the Greeks were pioneers in developing formal logic upon a sound basis, and in establishing the principles of mathematics, thereby performing a very great service to civilisation. In the history of human thought, we are faced with a paradox—that mankind learnt first how to reason correctly *from* given principles ; only later did he develop a method of finding out correct principles from which to reason. The history of the race is repeated in the life of the individual ; it is far easier to teach a young person the " rules of logic " than it is to implant in him a sound knowledge of the principles of induction. A valuable amount of " spade work " was done by the Greeks in the former direction ; and there is no doubt that some of their ideas and theories were also fruitful in providing starting points for comparatively modern scientific research.

References

Ida Freund, *The Study of Chemical Composition* (for this and many other chapters) : Camb. Univ. Press (out of print).

Westaway, *Scientific Method* (see ref. after Chap. I).

Whewell, *The History of the Inductive Sciences*, 3 vols.

Exercises on Chapter II

1. Write a short account (not more than 200 words) of Greek theories of matter, explaining why the Greeks failed to develop the study of natural science.

2. Discuss the position which deductive logic and mathematics occupy in science.

CHAPTER III

ALCHEMY

" Hence ! you are an alchemist, make gold of that."—
Timon of Athens.

We have seen that the principal weakness of the Greeks, from the point of view of Natural Science, was their neglect of experimental observation. The opposite criticism can be levelled at the Egyptians, who, during the time in which the Greeks were occupied with philosophy, were attaining considerable skill and knowledge in the working of metals, the manufacture of glass, soap, and many other substances. The name chemistry seems to have been derived from this.

" When the Greeks and Romans visited Egypt, they were impressed by the skill which the Egyptians showed in working metals and in similar operations, and called these various arts the ' Art of Egypt.' Now the Egyptian word for Egypt is *Kemi* . . . and means ' The Black Land '—no doubt in reference to the black colour of the mud left behind when the waters of the Nile receded after the yearly flood. The ' Art of Egypt ' therefore became the ' Art of Kemi,' and from Kemi we get our present word ' *chemistry*,' through the intermediate Arabic word *kimia*."—Holmyard, *An Elementary Chemistry.*

Egyptian " science " seems to have been purely empirical—that is to say, it was a collection of " rules of thumb " which were found to work in practice. It was not, in fact, science at all. These " arts " of the Egyptians and the theories of the Greek philosophers remained separate, no fusion of the two being attained.

The Romans contributed little or nothing to science; and the student of early chemistry must turn to the Arabs, who by their practical investigations did much to increase chemical knowledge, and by their acquisition of Greek manuscripts became familiar with the speculations which we have touched upon in the previous chapter. The doctrine of the four elements, for example, was retained by the great Geber, but modified by him so as to be more in accordance with the observed properties of metals.

During this time, and for many centuries after, the principal study of the "natural philosophers" was alchemy; and the history of alchemy is the story of one of the most curious phases of human thought. The subject is immensely complicated, being bound up inextricably with numerous religious conceptions, with astrology, and with all kinds of superstition; we can only attempt a brief summary of its main aspects.

It has been stated that alchemy was developed in China at least six centuries before it was introduced into Western Europe. Be that as it may, the earliest authentic work dealing with transmutation of metals of which we have definite knowledge appears to be a Greek papyrus discovered at Thebes, and dating from the third century A.D. It is a straightforward document, dealing principally with methods of falsifying metals so that they might look like gold; a useful art, but hardly one upon which to found a philosophy.

However dubious its origin, alchemy soon assumed far larger pretensions. It claimed, not to falsify metals, but actually to change them into gold. In so far as this claim possessed any theoretical justification, it was this: Aristotle taught that the varieties of matter owed their differences to the presence in them of varying proportions of certain "elements"; change these proportions, and you will obtain a different kind of matter. There was nothing, therefore, theoretically impossible in the transmutation of base metals into gold. In accordance with

the general mystical tendencies of the time, a parallel was drawn between the animate and inanimate worlds. Nature strove towards perfection in both ; in the former, her noblest creation was Man ; in the latter, gold. Hence to convert lead into gold was to assist Nature in her struggle from the base to the noble, an operation worthy of the highest efforts of a philosopher, and possessing at the same time considerable pecuniary advantages.

This transmutation, of course, was effected by means of the famous " philosophers' stone." We hear many times of alchemists who possessed this stone, and of the wonders they performed ; we also hear of certain ingenious devices, such as hollow rods containing gold dust, and sealed at one end with wax, with which the molten contents of crucibles were stirred. A little gold dust was thus made the means of conjuring a good deal more from the pockets of credulous patrons.

In later times, the powers and claims of the alchemists became still further magnified. Astrology and Magic played their part ; and the alchemists veiled their researches in a cryptic language which was designed to mislead the vulgar and to intensify the mystery and importance of their researches. The philosophers' stone was declared to be capable not only of transmuting metals, but to be an universal elixir which could heal all diseases, and even prolong life indefinitely. It is not observed that any of the alchemists ever succeeded in this latter respect ; in fact, many of them came to a premature end. The supply of the philosophers' stone had an awkward habit of running out.

As to what constituted this invaluable stone, it is difficult to find any precise evidence. There are many accounts of its appearance. According to Böhme, it was a " very dark disesteemed stone, of a grey colour." Elsewhere it is described as a red powder. A certain theosophical sect, known as the Kabala, maintained that the

first alchemist was Adam himself; God revealed hidden truths to him, which were afterwards handed down by tradition. Hence we even find the Stone identified with the red earth of which Adam was made. In the nineteenth century, an expounder of "Occult Science," Êliphas Lévi, declared that the philosophers' stone is "no other than an universal magnet, formed of the Astral Light condensed and fixed about a centre. It is an artificial phosphorus, etc. . . ."

Amid the world of dreams, even of nightmare, inhabited by the alchemists, it would be vain to look for the growth of anything in the nature of scientific inquiry. A final quotation from an anonymous German work, published at Frankfort in 1686, will give some idea of the condition of alchemy at this period:

"Arathron commands over forty-nine visible regions. He is the celestial spirit of Saturn; he can operate natural things prepared by astrological influences. He changes treasures into coal and coal into treasures. He teaches alchemy and natural philosophy. He teaches the discovery of lead, its manipulation, and its change into gold. He must be invoked on a Saturday, at the first hour of sunset in the increasing moon."

It seems, in short, futile to deny that the spirit which animated the mediæval alchemists was utterly remote from that of present-day scientific investigation; or that their actual results, judged from a scientific standpoint, were negligible compared with those that have been obtained in the last three centuries. Some, of course, declare that it is a mistake to judge alchemy as though it were really concerned with chemistry at all; they say that it was a mystical "Science," of ancient origin, which used chemical terms in order to transmit some hidden wisdom to the initiated. It seems more than doubtful whether such a view can bear examination; but in any case, if alchemy had this significance, it has no bearing upon science in the modern sense.

This brief and necessarily sweeping review of the mediæval period has, of course, omitted the greatest achievements of that period, which lie altogether outside our province. The Middle Ages produced many marvellously beautiful things: great literature, great architecture, great sculpture. It may be that what we of the present generation have gained in one way we have lost in another; but it is useless to lament the changes which have occurred. The most striking characteristic of the present age is the advance of scientific knowledge; an advance which shows no sign of slackening in its rate of progress. We have chosen our path, and must follow it, even though we do not know where it will eventually lead us. It is foolish to declare that those who have gone before us, and who saw life with other eyes, accomplished nothing; but it is equally foolish to attempt to put back the clock, and in a burst of regret for past glories to belittle the successes which have been patiently won in the study of Nature during the last few hundred years.

References

Most histories of chemistry give some account of alchemy. The reader who wishes to find a scholarly examination of the mystical pretensions of alchemy may consult *The Secret Tradition in Alchemy*, by A. E. Waite (Kegan Paul).

Exercise on Chapter III

Discuss the statement "Alchemy bears the same relationship to chemistry as astrology bears to astronomy."

CHAPTER IV

THE RENAISSANCE, AND THE DAWN OF MODERN CHEMISTRY

" It is now time to consider not of how many Elements it is possible that nature may compound mixt bodies, but (at least as far as the ordinary experiments of Chymists will inform us) of how many she doth make them up."—Boyle, *The Sceptical Chymist.*

One of the main difficulties in dealing briefly with the early development of chemistry is that it is impossible even to mention all the factors which led finally to its spectacular progress during the nineteenth century ; for one branch of science is not independent of another, and science as a whole is only part of the mass of contemporary human thought. The chemical historian is strongly tempted, as are other historians, to divide his subject into " periods " ; this has the advantage of emphasising the principal aspects of the subject, but may lead the student to imagine that its progress was far more logical and orderly than is in fact the case ; it also leads almost inevitably to the suppression of much important work which does not happen to bear directly upon the principal subject of the " period " in question. For example, the doctrines of the alchemists flourished in certain quarters for some time after chemistry had passed out of the " alchemical period " ; again, the progress of chemistry would not ultimately have been so rapid if it had not been for the development of physics in the seventeenth and eighteenth centuries, though it

was not until much later that the concepts of physics were introduced to any great extent into chemistry.

We are forced to adopt in this book a rough division of chemistry into periods, and must merely warn the student that this gives only a partial view of the whole subject.

Alchemy reached its climax about the fourteenth and fifteenth centuries. Later, certain workers, though strongly tainted with alchemical doctrines, broke free to some extent from the futile pursuit of the philosophers' stone, and enriched chemical knowledge in the field of medicine. Chief among these were Aureolus Phillippus Theophrastus Bombastus von Hohenheim, known for short as Paracelsus (1493–1541), and van Helmont (1577–1644). This period of "Iatrochemistry," or medical chemistry, lasted roughly throughout the whole of the sixteenth and seventeenth centuries. We still have to wait, however, until chemistry began to be studied for its own sake, with no ulterior motive.

But meanwhile things were stirring. The Renaissance spread through Europe, bringing with it a general desire for knowledge of all kinds, and a spirit of free inquiry unfettered by scholastic and theological doctrines. In 1561 was born Francis Bacon, who merits an immortal place in the history of science. He exposed the current practices to the most devastating criticism—"observation careless, irregular, and led by chance"; "experiment blind, stupid, vague, and prematurely broken off"; "natural history trivial and poor"—strong comments these, but amply deserved. Then, in a great passage in the *Novum Organum* (1620), he lays down the procedure which should be followed:

"There are and can be only two ways of searching into and discovering truth. The one flies from the senses and particulars to the most general axioms, and from these principles, the truth of which it takes for settled and immoveable, proceeds to judgment and to the discovery of middle axioms.

And this way is now in fashion. The other derives axioms from the senses and particulars, rising by a gradual and unbroken ascent, so that it arrives at the most general axioms last of all. This is the true way, but yet untried."

These remarks are so clear that they call for little comment. If the reader has followed the substance of the preceding chapters, he will see that the first way is essentially that of deduction, the method followed, for example, by Aristotle in his "proof" of the theory of the four elements. The second way is that of induction, the method pursued by modern science. In consequence of his forcible exposition of these principles, and of his criticism of the Aristotelian methods as practised by his contemporaries, Bacon has been sometimes called the Founder of the Inductive Method. We have seen that Aristotle had perceived the possibility of induction, but unfortunately had not used it; nor had it been put into operation by his successors.

Almost contemporary with Bacon, in England and on the Continent, other powerful writers were arising who criticised the corrupt Aristotelian philosophy, and emphasised the importance of experiment. In fact, we have reached the birth of modern science. In a book of this size it is impossible to attempt a review in proper perspective of the events which now crowded in upon one another.

The movement had begun, and continued irresistibly, in spite of ecclesiastical opposition. In 1543 Copernicus published his work on the revolution of the earth round the sun. About a century later, Galileo established the laws of motion, and performed his celebrated experiment from the leaning tower of Pisa probably in 1590; this experiment showed that, apart from the resistance of the air, a light body fell to the earth at the same rate as a heavy one, thus disproving a dogma of Aristotle which had been placidly accepted by everybody for 2,000 years.

In 1687 Newton published the *Principia*, in which he showed that the orbits of the planets could be calculated from the laws of motion and from the "universal law" that the gravitational attraction between two bodies varies inversely as the square of the distance between them. These are the only hints we can give of the enormous progress being made at this time in mechanics and astronomy. Matters hitherto treated in a vague and qualitative manner were now reduced to precise calculation; and the inductive method was triumphing in a manner little short of miraculous. The effect upon contemporary human thought was profound; the popular feeling is summarised in the couplet of Alexander Pope:

> "Nature, and Nature's laws, lay hid in night;
> God said, 'Let Newton be!' and all was light." *

But we must turn back to chemistry; and we find we have still to wait a long time before we can observe really rapid progress. We must, however, notice briefly a most remarkable book, the *Sceptical Chymist* of Boyle, published in 1661. The Hon. Robert Boyle, who has been described as the "father of chemistry, and brother of the Earl of Cork," was the first president of the Royal Society of London for Promoting Natural Knowledge. In 1662, the year in which this now world-famous society was formally incorporated by Charter of Charles II, Boyle announced the discovery of "Boyle's Law." He carried out remarkable researches in almost all branches of physics and chemistry; and, according to some, there is "nothing in the literature of these sciences to surpass, or even to equal them" (Freund, *loc. cit.*). *The Sceptical Chymist* is a masterpiece of critical analysis.

* We cannot forbear quoting a second couplet, the work of J. C. Squire:

> "It did not last: the Devil, howling '*Ho!*
> *Let Einstein be!*' restored the status quo."

Written mainly in the form of an argument between Themistius, a typical Aristotelian natural philosopher, and Carneades the sceptic, who is Boyle himself, it attacks the very foundations on which contemporary chemistry was built. Carneades asks for definite evidence as to the nature of the elements, which he defines as *substances which cannot be split up into anything simpler.* He will not be put off with a mere exposition of the beauty and " logical coherence " of the Aristotelian system ; he asks for experimental evidence which shall *show* that material bodies in general really are compounded of the so-called elements, whether these be earth, air, fire, and water, or the salt, sulphur, and mercury of Paracelsus. Almost the only evidence which Themistius can bring forward is the behaviour of a piece of wood, when it is burnt. There is obviously fire ; there is smoke, which disappears, and is therefore air ; there is water, because it comes out of the wood, and hisses ; and the ash which remains represents earth. Hence, since these four elements can be obtained from wood by the action upon it of fire, it was argued that they must have been present, compounded together, in the wood. Fire, it was generally agreed, was a " great resolver of bodies," *i.e.* its action was to break bodies up into simpler substances, in this case the four elements.

Themistius rather despises his own example ; he remarks disdainfully that " if men were as perfectly rational as 'tis to be wished they were, this sensible way of probation " (*i.e.* testing the theory by experiment) " would be as needless as 'tis wont to be imperfect. For it is much more high and philosophical to discover things *a priore* than *a posteriore*. . . . And indeed they (the Aristotelians) employ experiments rather to illustrate than to demonstrate their doctrines." Here the classical attitude of the " Schoolmen " is remorselessly dragged into the light ; its features, as we have before observed, are a blind worship of deductive logic ; the belief that

by sufficient exercise of the reasoning faculties the truth could be deduced, without recourse to actual investigation, from a few basic principles ; and a lofty contempt for those who prefer to discover the facts first and to reason about them afterwards. Themistius indeed refers to active experimenters as " sooty empirics " ; the Aristotelian doctrines (note that they are *doctrines*, rather than theories) are so perfectly logical that no really rational person could fail to perceive that they must be true ; but if Carneades is so vulgar as to demand a practical illustration of their truth, he shall have it. So the burning wood is brought forth, in the confident expectation that Carneades will now be satisfied and convinced.

But Carneades refuses to be convinced. He puts forward the entirely original and unexpected objection that because these four things can be obtained from wood by the action of fire, it does not prove that they were pre-existent in the wood. The company is " not a little surprised " at this, for it had always been assumed as self-evident that nothing could be obtained from a thing which did not previously exist in it. One of his hearers, Philiponus, mildly rebukes him for trying to be merely paradoxical, and asks if, for instance, when a refiner mixes gold and lead, and then cupels the mixture (*i.e.* heats it in a blast of air), thereby separating it into " pure refulgent gold and lead," any man can doubt that gold and lead existed in the mixture before it was committed to the fire. Carneades has two things to say in answer to this. In the first place, he points out that any one can see a refiner mix his gold and lead beforehand, but no one has ever seen Nature " pull down a parcel of the element of fire " and mix it with earth, air, and water to obtain a " mixt body." And in the second, on cupelling a mixture of gold and lead, we obtain gold and litharge, the latter being " lead indeed, but such lead as is differing in consistence and other qualities from what it was before."

In spite of the way the Aristotelians were routed in this book, Boyle's ideas failed to make much immediate impression. The main reason for this was that he was so greatly in advance of his age that the importance of his arguments was not fully appreciated by his contemporaries. Chemistry had to progress for another hundred years before reaching a satisfactory experimental method of demonstrating that a given elementary substance really was an element, and that though it might undergo various modifications, it could not be resolved into anything simpler. Boyle himself was unable to suggest a means; and the book ends, as it begins, on a note of scepticism.

"And (concludes Carneades smiling) it were no great disparagement for a sceptick to confesse to you, that as unsatisfyed as the past discourse may have made you think me with the doctrines of the Peripateticks, and the chymists, about the elements and principles, I can yet so little discover what to acquiesce in, that perchance the inquiries of others have scarce been more unsatisfactory to me, than my own have been to myself."

References

Whewell, *loc. cit.*
Boyle, *The Sceptical Chymist* (Everyman Library).

Exercises on Chapter IV

1. Rewrite the quotation from Bacon (p. 24) in your own words, taking one example of each of the "two ways of discovering truth."

2. Write a short account of Boyle's criticism of the Aristotelian philosophers.

PART II

CHEMISTRY BEGINS TO BECOME AN EXACT SCIENCE

INTRODUCTION

"Chemistry only took rank as a science when it made quantitative work its basis."—FREUND.

BOYLE, for all his shrewdness, was unable to progress very far; we have seen that his criticisms were destructive in the main. During the next hundred years or so, some advance was made, however, in the application of quantitative measurement to chemical problems. Up till now, the study of chemistry had been entirely qualitative. To take a very simple instance of the difference between a qualitative standpoint and a quantitative, we may consider them both applied to the density of a substance. A certain metal may be heavy, such as lead, or light, such as aluminium. The words "heavy" and "light" describe qualities which the two metals possess; they do not answer the question "How heavy?" or the similar query "Heavy or light compared with what?" We make a further important step when we answer these questions, and introduce the *density* of the substance, measured in definite units. Again, certain substances may be loosely described as "soluble" or "insoluble" in water; these are qualitative terms once more. The modern scientist goes further, and *defines* solubility as the number of grams of the substance which will dissolve in 100 grams of the

solvent to make a saturated solution at the temperature considered.

This transition from qualitative description to quantitative measurement may not appear very important to the layman; but it is actually the very essence of modern science, as we have mentioned in the first chapter of this book; and the progress which has followed in the past consequent upon this transition is nowhere more clearly shown than in the history of chemistry.

The alchemists and their contemporaries had been chiefly concerned to describe such properties of substances which appealed directly to the senses, such as colour, consistency, and so forth. It had not occurred to them that any useful purpose could be served by weighing substances before and after a chemical reaction.

But the advances which took place in physics, astronomy, and allied sciences during the sixteenth and seventeenth centuries—advances due to the combination of the inductive method with quantitative measurement—could not help having a repercussion upon chemistry. This is not a history of chemistry as a whole, and we can only afford space to mention the more important work which was done up to the time when Dalton's theory was published, hoping thus to give the student some idea of the general state of chemistry at the beginning of the nineteenth century. This work may be roughly grouped under three heads:

(I) Theories of combustion, and the establishment of the oxygen theory by Lavoisier; together with a discussion of the Law of Conservation of Mass.

(II) The Law of Constant Proportions, and the controversy between Berthollet and Proust.

(III) Black's work on the alkalies, and the Law of Reciprocal Proportions, or the Law of Equivalents.

Since Lavoisier's work in overthrowing the theory of phlogiston is generally admitted to be one of the most striking combinations of quantitative methods with inductive reasoning, we shall treat of (I) at some length, and of (II) and (III) rather more briefly. Further, we may depart occasionally from strict historical sequence ; the controversy between Proust and Berthollet, for example, lasted well into the nineteenth century, by which time the truth of the Law of Constant Proportions was accepted by the majority of chemists. Again, we shall mention briefly, in connection with the Laws in (I) and (II), some of the more recent work performed in this field ; this work has served to confirm the Laws to a degree of accuracy impossible to the older chemists who propounded them.

CHAPTER V (A)

THEORIES OF COMBUSTION

" One of the most interesting chapters in the history of chemical science is that dealing with the study of the phenomena of combustion and their interpretation. It lends itself specially well to the purpose of showing within the scope of not too complicated phenomena, how a theory arises, how it is applied, how the conservatism inherent in the human nature is reluctant to give up an accustomed interpretation of nature, even when it no longer answers to the first requirements of a theory, that is, when it no longer explains the facts and laws observed in the class of phenomena to which it refers ; but how after all facts are and always must be the strongest, and hence how a theory is finally given up when no longer able to deal with the facts, and how its place is then taken by another better fitted to do so." —FREUND, *The Study of Chemical Composition.*

THE " Phlogiston " Theory was the dominant theory of combustion during the eighteenth century. It was the product of two men, Beccher (1635–1682) and Stahl (1660–1734). The central idea of the theory may be stated quite simply as follows :

When a substance burns, something escapes from it into the surrounding atmosphere.

This idea, it will be seen, is not entirely unlike that of the ancients and the alchemists, namely, that the action of fire is to break up substances into simpler bodies. Beccher, the founder of the theory, expressed himself somewhat vaguely on the subject ; according to him, all combustible substances had in them a " principle of combustibility," and when metals, in particular, were

calcined, "the more volatile part" was "expelled." It remained for Stahl later to give these views more precision, and to apply them more directly to actual cases.

Stahl named this "combustible principle" *phlogiston*, from the Greek verb which means "to set on fire." According to him, the combustion of any substance, whatever its nature, could be described as in the following examples:

Metal, on combustion = *calx* + *phlogiston*.
Sulphur, on combustion = *sulphuric acid* + *phlogiston*.

(The distinction between sulphurous and sulphuric acids, and between acids and their anhydrides, was not clear at this time; carbon dioxide, for example was called carbonic acid or carbonic acid gas indifferently; nowadays, of course, the former term would refer only to an aqueous solution of carbon dioxide.)

(It will be convenient in what follows to denote phlogiston by the symbol ϕ.)

Stahl also explained the reverse process, namely, the reduction of a metallic calx by heating it with carbon, by supposing carbon to be a substance rich in phlogiston. When carbon converts a calx into a metal, it supplies phlogiston to the latter, thus reversing the process of combustion.

Calx	+	*carbon*	=	*metal*
(no ϕ)		(rich in ϕ)		(contains ϕ)

We now come to an interesting application of the theory. Zinc calx, like other calces, contains no phlogiston; sulphuric acid, as we have seen above, also contains no phlogiston (since it is obtained by burning sulphur). Zinc calx dissolves in sulphuric acid, to give the salt "white vitriol" (zinc sulphate). Hence, since white vitriol is derived from two substances, neither of which

contains phlogiston, white vitriol cannot itself contain phlogiston. As an equation,

Zinc calx	+	*sulphuric acid*	=	*white vitriol*
(no ϕ)		(no ϕ)		(no ϕ)

Now if, instead of zinc calx, we take metallic zinc, we find that it also dissolves in sulphuric acid, to give the same substance, white vitriol. But, since white vitriol contains no phlogiston, and zinc *metal* does, the phlogiston must escape somehow when the zinc dissolves in the acid. This was strikingly borne out by the facts; when zinc dissolves in sulphuric acid, a light, highly inflammable gas is evolved, in contrast, of course, to the behaviour of the zinc calx, which dissolves without any evolution of gas. This gas was called "inflammable air" by Cavendish, who was the first effectively to isolate the gas and to describe its properties. The equation for the above action was therefore:

Zinc	+	*sulphuric acid*	=	*white vitriol*	+	*inflammable air*
(contains ϕ)		(no ϕ)		(no ϕ)		(contains the ϕ originally in the zinc)

Inflammable air was consequently especially rich in phlogiston, and was thought by many to be virtually pure phlogiston. As was to be expected, it possessed powerful reducing properties.

It is clear that we have here a most ingenious theory, which fulfils the requirements of a good scientific hypothesis—it accounts for a number of apparently unrelated facts, linking them together by means of one common explanation. Nevertheless, a number of other facts gradually accumulated which were not at all easy to reconcile with the phlogiston theory. The chief of these were:

(*a*) *Metals, on calcination, increase in weight; if phlogiston were like any other known material substance, its escape from a body should leave that body lighter than before, and not heavier.*

There were various attempts to explain this increase in weight; some did not attempt to explain it, but said that it was of no significance. Even with due regard to the fact that changes of weight were not given the prominence which is now assigned to them, the attitude of these persons can only be compared to that of the proverbial ostrich.

The principal explanations suggested were as follow:

(i) During combustion "fiery corpuscles" entered the burning substance, probably through the containing vessel, thus adding to its weight. This theory was put forward by Boyle among others, but was finally disproved by Lavoisier (*vide infra*).

(ii) The increase in weight was due to the difference in density between the calx and the metal. This was a somewhat confused application of Archimedes' principle, which could easily be shown to be fallacious.

(iii) Phlogiston weighed less than nothing; hence *loss* of phlogiston meant an *increase* in weight. This explanation, which appears to us somewhat fantastic, was nevertheless one of the most plausible. Let us imagine ourselves for the moment to be ardent phlogistonists, advancing the following arguments:

> There is no *logical* absurdity in the idea of a substance being repelled upwards, instead of being attracted downwards, by the earth.
>
> Flames, which may be escaping phlogiston, travel upwards.
>
> "Inflammable air," which may be phlogiston itself, also travels upwards.
>
> The phlogiston theory has explained so many apparently disconnected facts—*e.g.* combustion of metals and non-metals, reduction of metallic calces by carbon (and also by inflammable air), and the behaviour of metals and their calces with acids—that there *must* be

truth in it, even if it involves consequences startling at first to common sense.

The reader may amuse himself by meeting these arguments in turn.

(*b*) *Air is necessary for combustion.*

This fact was known, as well as (*a*), by Geber in the eighth century; Boyle showed that sulphur will not burn in a vacuum, and Stahl that calcination is not possible in a vacuum, or, completely, in a closed vessel.

This was explained by supposing that the escaping phlogiston needed something to absorb it, the air acting towards phlogiston like a sponge taking up water. There is, of course, one almost overwhelming objection to this explanation; the residual air, after a substance has been burnt in it, has a smaller volume than the original air; hence absorption of phlogiston means a contraction in volume. Scheele (1742–1786) knew this, and recognised it as a serious difficulty. He pointed out that the residual air was lighter than ordinary air, which confirmed the supposition that phlogiston had a negative weight; but the "lost air" (*i.e.* the gas which had disappeared) worried him considerably, as well it might.

In the year 1774 there appeared some investigations by John Priestley (1733–1804) which were of the first importance, since they described the properties of the gas we now know as oxygen. Actually, this gas had been obtained by Scheele a few years earlier, but his results had not been published. Priestley obtained the new gas by heating the red calx of mercury. He stated that "a candle burned in this air with a remarkably vigorous flame." A mouse, shut up in a certain volume of it, lived twice as long as in the same volume of ordinary air. He breathed some himself, and felt his breast "peculiarly light and easy for some time afterwards." Some of his suggestions as to the uses to which the gas

might be put have been adopted; for example, its use in the treatment of pneumonia, and for obtaining high temperatures.

Priestley was a devout minister of religion, as well as a scientist. Consequently he had to account for two things, namely, why this gas, which appeared to be a superior kind of air, should not have been provided instead of ordinary air by a beneficent Providence; and also, how it was that this air was produced from mercury calx. The former problem he solved by remarking that if ordinary air were all composed of this gas, we might "live out too fast in it," and, further, that "the air which nature has provided for us is as good as we deserve." The second he explained by means of the phlogiston theory, in the following manner:

Mercury calx, unlike other metallic calces, gives the metal on heating *alone;* it does not need the presence of carbon. From whence does it obtain the phlogiston necessary for this conversion? The answer, surely, is "from the air." Ordinary air must contain some phlogiston, since things are constantly burning in it and giving out phlogiston while they burn. Hence, when mercury calx is heated, the following change takes place:

$$\underset{(\text{no } \phi)}{\textit{mercury calx}} + \underset{(\text{contains some } \phi)}{\textit{ordinary air}} = \underset{(\text{contains } \phi)}{\textit{mercury}} + \underset{\textit{its phlogiston}}{\textit{air deprived of}}$$

Now, the air thus deprived of phlogiston would be far more ready to take up phlogiston again than ordinary air, which already contains phlogiston, just as a dry sponge will soak up more water than a sponge which is moist. In other words, the air obtained in the above action should be a very good supporter of combustion; in fact, we should expect it to possess just those properties which Priestley described. Priestley was quite satisfied with this explanation, and called the new gas "dephlogisticated air."

In case the student has not perceived it for himself, we

may point out that the phlogiston theory can similarly account for the gas we now call nitrogen. If a candle is burnt in a limited supply of air, it eventually goes out, and the residual air will not support combustion. This was explained, of course, by supposing that the air surrounding the candle flame had become saturated with phlogiston, and would not take up any more.

To sum up the main achievements of the phlogiston theory, it provided a consistent explanation of the following phenomena :

Conversion of metals and non-metals into calces and acids respectively.

Reduction of metallic calces by carbon and inflammable air.

Production of inflammable air when a metal such as zinc dissolves in an acid, as contrasted with the non-production of inflammable air when a calx dissolves in an acid.

Production of " phlogisticated air " when a substance is burnt in ordinary air ; and the production of " dephlogisticated air " when mercury calx is heated.

The main facts which called for somewhat far-fetched explanations on the phlogiston theory were :

The increase in weight of substances on calcination.

The fact that air, when it becomes " phlogisticated," occupies a smaller volume than the original air.

The year 1774 was an eventful one in the history of chemistry, since it saw also the publication of a memoir by the French chemist, Antoine Laurent Lavoisier, on " The Increase in Weight of Metals on Calcination." Lavoisier was the son of a rich aristocrat, who had spared no expense in providing his gifted child with the best education possible. When only twenty-one, the young Lavoisier had been awarded a gold medal for devising

the best and most economical method of lighting the streets of Paris. This indicates that he had, among other things, practical ability; and his genius was indeed of extraordinarily wide range, the acuteness of his reasoning and his industry as an experimentalist being manifest in the vast number of papers on physical and chemical subjects which he published in his lifetime.

In the memoir under consideration, written when he was thirty-one, Lavoisier set himself to examine the cause of the increase in weight of metals on calcination, with particular reference to the theory mentioned above, namely, that this increase was due to fiery matter entering the vessel. He began by reasoning that if this were the cause, then, by calcining the metal in a *closed* vessel, the whole vessel should weigh more at the end of the operation than before, the weight "being augmented by that of the whole quantity of fiery matter which had been introduced during calcination." The second part of his argument shows that he was (unlike the Phlogistonists) disposed to consider that combustion was due to combination of the combustible body with some portion of the air; for he argues, that if this is so, "the whole vessel after calcination" (while still sealed up) "must be no heavier than before, and must merely be partially void of air, and the increase in weight of the vessel will not occur until after the air required has entered." Hence, if the experiment with a sealed vessel is performed, according to the former theory (that of the entry of fiery matter) it should increase in weight; according to the latter (combination of air with the metal) there should be no alteration in weight.

This experiment Lavoisier proceeded to carry out. He proceeded as follows:

Two equal weights of tin were taken, and placed in two retorts of unequal size, one being much larger than the other. Each retort was weighed, with the tin it contained.

He then heated the retorts, sealed them off, allowed them to cool to room temperature, and weighed again. (This was

necessary, as if the retorts had been sealed at room temperature, they would have burst on heating.)

The retorts were then heated over a coal fire until no further chemical action occurred (the formation of calx on the surface of the tin was easily visible); cooled, and weighed.

The retorts were then opened. Air rushed in with a hissing noise; when this had ceased, the retorts were weighed again full of air.

Finally, the calx in the retorts, together with excess of unchanged tin (for there was more than enough tin to combine with the air in the retorts), was detached and weighed.

The essential results are given below (the weights are in grains).

	Small Retort.	Large Retort.
Weight of tin	4,608	4,608
Weight of retort+tin+air at room temperature	7,634·5	12,003·75

Retorts heated, sealed as described, cooled and weighed. Then placed in furnace until calcination was complete, cooled, and weighed.

Change in weight of sealed retort on calcination of the tin	—0·27	—1·00

This slight decrease in weight was within the limits of experimental error.

Weight of retort after opening to admit air at room temperature	7,637·63	12,013·81
Increase in weight due to air which entered	3·13	10·06

The partially burnt tin was then removed, and its weight compared with that of the tin originally taken.

Increase in weight of tin on partial conversion into calx	3·12	10·00

The last two sets of figures are plainly identical, within the limits of experimental error.

From the results of these experiments, Lavoisier drew the following conclusions :

(1) *In a given volume of air only a fixed quantity of tin can be calcined.*

(2) *This quantity is greater in a large retort than in a small one.*

(3) *The sealed retorts do not alter in weight during the calcination of the tin ; hence, the increase in weight of the metal does not arise from fire matter, nor from any other matter extraneous to the vessel.*

(4) *The increase in weight is due to combination of the metal with the air ; and the fact that this increase appears identical with the weight of the air entering after calcination shows further that the specific gravity of the air combining with the metal is approximately equal to that of atmospheric air.*

(Actually, the retort after opening at the end of the experiment will contain a larger proportion of nitrogen than before ; but the experiments were not of an accuracy sufficient to show any difference in the specific gravity of the gases present.)

Extremely important as these results were, they did not in themselves establish the nature of the portion of air absorbed during calcination. Light on this matter was to come from Priestley, who visited Paris in 1774, and told Lavoisier at dinner of the discovery of " dephlogisticated air," whereupon " all the company, and Mr. and Mrs. Lavoisier as much as any, expressed great surprise." * Lavoisier proceeded forthwith to apply this new discovery to the confirmation of his own views, and in the following year presented a memoir to the Académie des Sciences " On the Principle which combines with Metals during their Calcination, and which augments their Weight." Characteristically, he tested first whether the red mercury calx really was a calx, by heating it with

* Priestley's own account of the meeting.

charcoal. As with other calces, he obtained the metal and " fixed air " (carbon dioxide). He then investigated the properties of Priestley's gas for himself, and remarked : " It seems proved that the principle which combines with metals during their calcination . . . is no other than the purest portion of the very air surrounding us, which we breathe, and which in this operation passes from the expansive to the fixed state."

Even so he was determined to push the proof still further. In 1789 he published a *Traité de Chimie* in

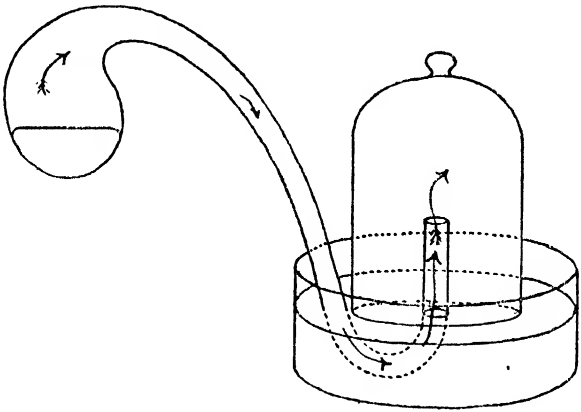

Fig. 1.

which he describes another experiment with mercury. (It has caused some heartburning, by the way, that in this treatise he speaks of the " air, which Dr. Priestley, Mr. Scheele, and I discovered about the same time.") This experiment was as follows :

4 ounces of pure mercury were placed in a retort of which the neck had been drawn out and bent upward so as to communicate with air in a bell-jar (see Fig. 1).

This mercury was heated for 12 days to a temperature just below the boiling point, after which no further calcination

was observed. The volume of the air in the bell-jar diminished up to this point and then ceased; and the residual gas would support neither life nor combustion.

On heating the mercury calx, the gas previously described was given off; and the volume of this gas so obtained was equal to the diminution of volume of the air.

Lavoisier also weighed the gas obtained: his actual figures in the experiment were:

Weight of calx formed	=45 grains.
Weight of mercury left after heating calx	=41·5 grains.
Difference	=3·5 grains.
Weight of gas given off from calx	=3·5 to 4 grains.
Diminution in volume of air in bell-jar	=7 to 8 cubic inches.
Volume of gas obtained from calx	=7 to 8 cubic inches.

Thus the loss in weight of the mercury calx on conversion to mercury was equal to the weight of the gas obtained from the calx; and the volume of gas which was absorbed when the mercury was converted to calx was equal to the volume of gas eventually recovered from the calx.

The conclusion naturally drawn was that "atmospheric air is composed of two elastic fluids of different and so to speak opposite nature." One of these gases combined with metals and other substances when they burnt in air; the other remained inert and took no part in the combustion.

To the gas supporting combustion Lavoisier gave the name "oxygen," or "acid-producer," since non-metals gave acids when burnt in it. (It was his erroneous view that all acids contained oxygen, an idea which led to chlorine being regarded for a long time as an oxide.) The other gas he called "azote" (unable to support life), a name by which nitrogen is still known in France.

It will probably seem to the reader that the results of

these experiments needed only to be published for Lavoisier's views to be accepted, so simple and convincing are they. Human nature being what it is, however, immediate acceptance was by no means general. Many of the older chemists, life-long adherents of the phlogiston theory, were unable to alter their accustomed standpoint. And there was one phenomenon which Lavoisier was for the time unable to explain. It will be remembered that one of the triumphs of the older theory was the explanation of the appearance of inflammable air when some metals were dissolved in acids; the phlogiston was supposed to be disengaged from the metal when the latter formed a salt. On the oxygen, or " antiphlogistic " theory, a salt is formed when a metallic oxide dissolves in an acid. (The formation of water at the same time had not been observed, a fact which was very natural, since excess of water was already present with the acid.) Whence, then, came the inflammable air when a metal itself was dissolved in an acid? A chemist less careful than Lavoisier might have concluded that a metal was a compound of a calx together with inflammable air, the latter being given off on salt formation; but Lavoisier saw the unlikelihood of this, since the metal weighed less than its calx. While recognising the difficulty, he wisely admitted it to be such, and left it unexplained for the time.

The clue came not long after, when Cavendish, in 1781, showed that when inflammable air burns in air, " almost all the inflammable air and about one-fifth part of the common air lose their elasticity, and are condensed into dew which lines the glass."

Told of this work by Sir Charles Blagden in 1783, Lavoisier at once saw its significance. Water, so long regarded as an element, was really a compound of inflammable air and oxygen; the former gas, after this discovery, was renamed hydrogen, or " water-producer." Lavoisier hastened to repeat Cavendish's experiment on

a larger scale; further, he passed steam over a red-hot iron wire, thus decomposing some of the steam; he showed that iron oxide was formed, and that hydrogen passed on and could be collected.

The action of metals and of their calces could now be satisfactorily explained as follows:

Metal + *acid* = *salt* + *hydrogen*
Calx (metallic oxide) + *acid* = *salt* + *water*;

in the latter case, the hydrogen of the acid combined with the oxygen contained in the calx.

In the years following, Lavoisier continued indefatigably to produce papers dealing with applications of the theory he had so brilliantly demonstrated. In 1789 came the French Revolution. Lavoisier, being one of the hated "farmers-general," and the possessor of valuable property which the Republican Government was only too anxious to confiscate, was eventually thrown into prison on a trumped-up charge. His end is eloquently described by Whewell:

"In his imprisonment, his philosophy was his resource; and he employed himself in the preparation of his papers for printing. When he was brought before the revolutionary tribunal, he begged for a respite of a few days, in order to complete some researches, the results of which were, he said, important to the good of humanity. The brutish idiot, whom the state of the country at that time had placed in the judgment-seat, told him that the republic wanted no sçavans. He was dragged to the guillotine, May the 8th, 1794, and beheaded, in the fifty-second year of his age—a melancholy proof that, in periods of political ferocity, innocence and merit, public virtues and public services, amiable manners and the love of friends, literary fame and exalted genius, are all as nothing to protect their possessor from the last extremes of violence and wrong, inflicted under judicial forms."

It is difficult to overestimate the effects of Lavoisier's work upon the development of chemistry. Whether or not

we entirely agree with Wurtz, in his famous dictum " La Chimie est une science française ; elle fut constituée par Lavoisier d'immortelle mémoire," the fact remains that he did far more than merely to overthrow an erroneous theory of combustion. Though he was not the first to attempt quantitative work in chemistry, the importance of such work was emphasised by him as it had never been before ; and the next few decades saw an amazing advance in the status of the science. Thomson, in his *History of Chemistry* (1831), says that Lavoisier was destined " to introduce the same precision, and the same accuracy of deductive reasoning (into chemistry) which distinguishes the other branches of natural science " (viz. physics, astronomy, etc.).

The phlogiston theory, after the discovery of the composition of water, was of course doomed. France, not unnaturally, was readily converted ; and the Berlin Academy followed in 1792. British chemists were more conservative ; Thomson writes (*loc. cit.*) :

" Mr. Cavendish new modelled the phlogistic theory, and published a defence of phlogiston which it was impossible at that time to refute. The French chemists had the good sense not to attempt to overturn it. Mr. Cavendish after this laid aside the cultivation of chemistry altogether, and never acknowledged himself a convert to the new doctrines.

" Dr. Priestley continued a zealous advocate for phlogiston till the very last ; . . . but Dr. Priestley, notwithstanding his merit as a discoverer and man of genius, was never, strictly speaking, entitled to the name of chemist ; as he was never able to make a chemical analysis. . . .

" Thus, soon after the year 1790, a kind of interregnum took place in British chemistry. . . . Dr. Black was an invalid, Mr. Cavendish had renounced the cultivation of chemistry, and Dr. Priestley had been obliged to escape from the iron hand of theological and political bigotry, by leaving the country."

It was only a pause ; and the great names were to be succeeded by one equally great, namely, the founder of

the atomic theory, as he is often called. Before dealing with this theory, however, we must briefly examine the establishment of the stoichiometric laws of chemical combination.

References

The *Alembic Club Reprints* (2*s*. 6*d*. each) contain reprints, in English, of the following original papers :

No. 7. " The Discovery of Oxygen." Part I. Experiments by Joseph Priestley, LL.D. 1775.

No. 8. " The Discovery of Oxygen." Part II. Experiments by Carl Wilhelm Scheele. 1777.

Thorpe: *Essays in Historical Chemistry* (Macmillan).

For a critical examination of Lavoisier's early work, see *The Eighteenth Century Revolution in Science—The First Phase*, by A. N. Meldrum (Longmans, Green and Co.).

Exercise on Chapter V (A)

Write an account, in not more than 600 words, of the theory of phlogiston, and of the experiments which led to its overthrow.

CHAPTER V (B)

THE LAW OF CONSERVATION OF MASS

" Nought then returns to nought, but parted falls
To *Bodies* of their prime Originals."
LUCRETIUS, *De Rerum Natura.*

" We might as well attempt to introduce a new planet into the solar system, or to annihilate one already in existence, as to create or destroy one particle of hydrogen."—DALTON.

THE Law of Conservation of Mass, in the form that " Matter is Indestructible," has been frequently assumed to be true from the earliest times in which thinkers bothered themselves about the nature of matter. By many it has been regarded as of the nature of an axiom, the truth of which need not be questioned. Anaxagoras, writing about 450 B.C., says: " nothing comes into being or is destroyed; but all is an aggregation of pre-existing things." It would be tempting to multiply instances, but the history of this law belongs rather to philosophy than to natural science, and we must confine ourselves to the aspects of it which concern chemistry more particularly.

For a precise conception of mass, the world had to wait until Newton, who drew a clear distinction between " mass " and " weight." Owing to the alteration in the gravitational field of the earth, the weight of a given body is not constant when it is moved from one place to another; it will be pulled more strongly towards the earth at the North or South Pole than it will be at the equator. But the *mass* of the body remains constant; it is measured by finding the acceleration produced in

the body by the action on it of a given uniform force, the mass being then inversely proportional to the acceleration produced. We can *compare* the masses of two bodies accurately by weighing them both *in the same place*. Mass was thus conceived by Newton and his successors as the true measure of the *quantity of matter* present in the body; and that is why the law is called the Law of Conservation of Mass, rather than the Law of Conservation of Weight.

As we have seen, Lavoisier was the first really to lay stress upon the importance of weighing in chemical experiments; and it is from him that we get a clear statement of the law, in the form that "Nothing is created, either in the operations of art or in those of nature, and it may be considered as a general principle that in every operation there exists an equal quantity of matter before and after the operation." This law he verified approximately in the particular cases of the calcination of tin, the decomposition of mercuric oxide, and some others; but in stating the law as a generalisation he, like others before him, was really expressing a fundamental *belief*, since the number of accurate analyses which he could quote in support of his statement was quite insufficient to justify the assertion of the law on a basis of pure induction. Since, however, everyone else was fully disposed to believe that matter could not be created or destroyed, this "general principle" was not disputed.

Possibly the reader considers all this as rather in the nature of hair-splitting. But in no case more than the one we are considering has there been a more general tendency to depart from what Bacon called "the true way," and to regard the Law of Conservation of Mass as an "axiom" of which no experimental proof is needed. Perhaps we all have a sneaking sympathy with Boyle's Aristotelian philosopher, when he said that "it is much more high and philosophical to discover things *a priore* than *a posteriore*." It is so much more impressive to

assert roundly that "The Sum Total of All the Matter in the Universe is Constant," than to say "When I burnt a piece of phosphorus in a closed flask, the whole thing seemed to me to weigh the same afterwards as it did before, as far as my not very accurate balance could show me." The latter statement, however, is scientifically sound; the former is an unprovable dogma.

Nevertheless, if we err in assuming too readily the truth of the law in its general form, at least we err in good company. Its truth has been assumed in practically every quantitative analysis that has ever been made; and it may be stated at once that in every analysis in which the total weight of the combining substances and the total weight of the products of reaction are available, the law has always been verified within the limits of accuracy of the particular analysis. In the following paragraphs we will give a few figures representing the results of some of the most accurate analyses of this kind which have ever been made, so that the reader can judge for himself to what degree of precision he may trust the law.

Every one who has read any account of analytical work in the past will have found the name of Stas, who did some very accurate determinations of combining weights. In some of these he weighed both the substances reacting and the product of their reaction; he did this, not because he doubted the truth of the law of conservation of mass, but because he assumed its truth, and wished to check the accuracy of his analyses. Some of his results are given below.

Synthesis of silver iodide. (Weights in grams.)

(A.) Sum of weights of silver + iodine.	(B.) Weight of silver iodide.	Percentage difference between (A) and (B).
60·0888	60·0860	− 0·0046
86·6687	86·6653	− 0·0039
82·8394	82·8375	− 0·0023
296·6300	296·6240	− 0·0020

Preparation of Silver Iodate.

This was prepared by two different double decompositions; weighed quantities of the iodate were then decomposed by heat, both the silver iodide produced and the oxygen evolved being weighed.

The percentage differences between the weights of iodate, on the one hand, and of iodide + oxygen on the other, were

$$+0{\cdot}0014 \quad \text{and} \quad -0{\cdot}0013.$$

The difficulties involved in conducting analyses of this order of accuracy are seldom realised. Stas's own account of the washing of silver iodide in the former set of experiments may help to do this:

"I have been obliged to do the washing at a high temperature and . . . in a dark room. Further, . . . I have been obliged to continue the washing day and night until completed, with the temperature slowly and steadily rising. But however rapidly one may perform the operation, as soon as the weight of the iodide exceeds 100 grams, forty-six to sixty hours of uninterrupted work are necessary in a dark room, the air of which becomes heated and damp from the vapours of the water bath. It is evident that such work soon exceeds human power, and that it is impossible to repeat it a large number of times."

The reader will probably agree with this moderate conclusion.

In 1895 Morley, in the course of investigations upon the composition of water—work which took him about twenty years—caused 30·3429 grams of oxygen to combine with 3·8211 grams of hydrogen:

Weight of oxygen + hydrogen	= 34·1640 grams	
Weight of water obtained	= 34·1559 ,,	
Difference		0·0056 per cent.

In 1893, as the result of some observations made by Heydweiller, H. Landolt began a series of investigations *with the express object* of verifying the law of conservation

of mass with the greatest possible accuracy. He chose for this purpose certain reactions which take place in solution with little evolution of heat, *e.g.* the reduction of silver sulphate to silver by ferrous sulphate. The two solutions were sealed in separate limbs of a Jena glass U-tube (Fig. 2), the whole tube being counterpoised with a similar tube (to reduce various errors—compare Regnault's method for determining gaseous densities); a

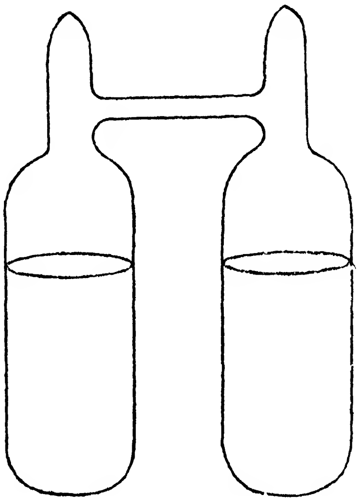

FIG. 2.

balance being used capable of detecting a change in weight of 0·0001 gram, with a load of 1 kilogram on each pan. The solutions were mixed, and the tube reweighed. At first a small decrease in weight was always found; this decrease amounted in some cases to as much as 1·5 milligram. This was finally traced to two causes: first, the slight evolution of heat drove off some of the moisture which always condenses as an invisible film even upon "dry" glass: and second, the vessel expanded and did

not return to its original volume for a long time. Both these effects of course diminished the apparent weight. After long standing, the original weight was regained to within the limits of experimental error, which was here 1 part in 10,000,000.

It must be remembered that the verification of the law to this degree of accuracy has only been done in certain special cases; and, in particular, these cases are all those in which the heat effect was small.

As the result of the foregoing, and of other analyses generally, we may therefore state the law of conservation of mass in the following form:

> In all chemical reactions hitherto studied, no difference has ever been observed between the total weight of the reacting substances and the total weight of the products of reaction, which cannot be put down to experimental error. In certain cases, this experimental error is extremely small.

This is a modest and unassuming statement; but it is safe.

NOTE ON THE PRECEDING CHAPTER

The Law of Conservation of Mass has been fundamentally modified since the recent discovery that energy possesses mass; the consequence of this is that in any transformation involving evolution of energy, a portion of the mass of the system is carried off, as radiation. The Laws of Conservation of Mass and of Conservation of Energy may be replaced by a single statement as follows:

When a system undergoes a change, the sum total of mass + energy in the system remains constant.

The following figures, taken from *The Universe Around Us*, by Sir James Jeans, may be of interest:

The amount of mass associated with energy is exceedingly small, amounting to 1 gram per 9×10^{20} ergs. Nevertheless, in certain radioactive changes, in which much energy is

released, the loss of mass due to radiation may be considerable. It has been estimated that when 1 ounce of uranium finally breaks down into helium and lead, 0·0002 oz. goes off in the form of radiation (roughly 1 part in 4,000).

In ordinary chemical changes the difference in mass between the initial and final products is extremely small. Thus, when good coal is burnt in oxygen the total weight of the products of combustion amounts to 99·999999994 per cent. of the initial weight of oxygen + coal. Differences of this order are, of course, far too small to be detected by chemical analysis.

The Law of Conservation of Mass, in the form in which we have stated it, therefore still holds good as a generalisation from experience; but we no longer believe that it is absolutely accurate.

References

References to Stas's analyses will be found in most of the larger works on chemistry.

Morley's work is published in full in the *Smithsonian Contributions to Knowledge*, XXIX. If the student has access to a library containing this volume, he is strongly advised to read Morley's account of one of the most masterly researches in the history of science.

Landolt's work appears in the *Zeitschrift für Physikalische Chemie*, Vol. 12, p. 1 (1893).

Exercises on Chapter V (B)

1. How far do you consider that Dalton's statement, quoted at the beginning of this chapter, is scientifically sound?

2. It is held by some physicists (*cf.* Jeans, *The Universe Around Us*, Cambridge University Press, 12*s.* 6*d.*) that in the stars matter may be undergoing destruction, being transformed into radiant energy (such as heat and light). What bearing have such views upon the Law of Conservation of Mass, as this is understood by chemists?

CHAPTER VI

THE LAW OF CONSTANT PROPORTIONS

THIS law may be stated as follows :

> *The same compound, however produced, always contains the same elements united together in the same proportions by weight.*

As with the law of conservation of mass, we seem face to face with a fundamental law of chemistry. If it were not true, chemical analyses would cease to yield concordant results ; there would be no precise meaning to be attached to the term " equivalent weight " ; and it is hard to see how the atomic theory could ever have been placed upon a secure basis.

Nevertheless, the law was not established without a struggle. It was clearly stated by Joseph Louis Proust (1755–1826) in 1799. Proust had found, for example, that copper carbonate, prepared by adding *either* potassium *or* sodium carbonate to a hot solution of copper in nitric acid, always had a constant composition. He found that

> 100 parts of copper always gave 180 parts of green carbonate.
> 180 parts of carbonate, on heating, always gave 10 parts of water, and 125 parts of black oxide of copper.

The same results, allowing for a small percentage of impurity, were obtained with the naturally occurring copper carbonates, the " malachites of Aragon." He concluded that the combining ratios of the constituents were fixed by natural law, and not " left to the power of chemists."

He recognised that two elements might form more than one compound, but stated correctly that when they did so the composition of each compound was perfectly fixed, the change in the combining ratios of the elements, from one compound to the other, being abrupt and considerable, and not gradual.

The truth of these statements was questioned by the eminent Frenchman Berthollet, chief chemist to Napoleon. Berthollet had been led by his own researches to a view of chemical action which did not harmonise easily with that of Proust. Berthollet had an acute and penetrating mind, of the kind which does not accept the current theories without question. He became a convert to the antiphlogistic theory in 1785; but he differed from Lavoisier, in that he did not regard oxygen as a necessary constituent of all acids, quoting sulphuretted hydrogen as an example of an acid containing no oxygen. In this we recognise that Berthollet was right, and Lavoisier wrong.

It would take too long to treat fully of the researches which led Berthollet to oppose Proust. Briefly, Berthollet had set himself to examine the work of Bergman, on chemical affinity, "affinity" meaning that property which causes two substances to combine together. Bergman had studied the manner in which various substances displaced one another from combination with other substances, and had drawn up as a result a table of "elective attractions" which was regarded as enormously important by contemporary chemists. The idea underlying this table was simple, and is still commonly used, though we realise now that we must make certain important reservations before we can apply it. For example, chlorine will displace bromine from potassium bromide, and bromine will displace iodine from potassium iodide. We say that chlorine has a stronger *affinity* for potassium than bromine has, and that bromine in turn has a stronger affinity for potassium than iodine has.

So we can range these elements in order of their affinities for potassium ; and when we have done so, we find that this order also holds good for their compounds with other metals. Again, iron will displace copper from copper sulphate ; so iron has a greater affinity for the sulphate radicle than copper has.

But the matter is not really as simple as this, as Berthollet was the first to show. He found that the displacement of one substance by another might depend also upon the relative amounts, or concentrations, of the substances present ; and that, by suitably altering these conditions, many reactions could be reversed. To take one example :

> Barium hydroxide + potassium sulphate give barium sulphate as a precipitate, potassium hydroxide being formed at the same time.

Therefore, according to Bergman's view of affinity,

> Barium has a greater affinity for the sulphate radicle than potassium has.

But Berthollet showed that, by boiling barium sulphate for a long time with potassium hydroxide solution, repeatedly renewing the potash, the reverse change

> Barium sulphate + potassium hydroxide = potassium sulphate + barium hydroxide

could be effected. Applying the affinity rule to *this* reaction, we should conclude that

> Potassium has a greater affinity for the sulphate radicle than barium has ;

which is directly contradictory to our previous one.

Further, Berthollet pointed out that the fact that one acid might displace another from combination with a metallic base did not really prove that the former acid

has a stronger affinity for the base. For example, we know that

Potassium chloride + strong sulphuric acid, on warming, give potassium sulphate and hydrogen chloride.

Phosphoric acid and potassium sulphate, heated *sufficiently*, give potassium phosphate and sulphuric acid.

But this does not prove that phosphoric acid is " stronger " than sulphuric, or that sulphuric acid is stronger than hydrochloric ; the displacement is due at least partly to the greater volatility of one of the two acids at the temperature of the experiment, which causes one of them to escape from the system altogether.

Here Berthollet had discovered a great chemical truth. The reader who has studied physical chemistry will realise that here is the germ of the Law of Mass Action. In all the above cases we are dealing with reversible reactions, which tend, if left to themselves, to set up an equilibrium in which the reacting substances and the products of their reaction all exist together. By altering the concentrations of the substances present we can alter the equilibrium. In particular, if by some means we remove one of the substances, the equilibrium will shift in such a way as to try to restore the substance we have removed ; and if we go on removing it, the reaction will proceed completely in one direction. Thus, in the first example we have quoted, the reaction proceeds in aqueous solution ; the barium sulphate, however, is almost completely removed from this solution by precipitation. Hence the reaction proceeds virtually to completion. But, by treating barium sulphate with a large excess of potassium hydroxide, and by removing the potassium sulphate and barium hydroxide which are formed, we can " drive the equilibrium " almost completely in the opposite direction.

These principles are now clearly understood ; but the mistake which Berthollet made was to suppose that the

compounds *themselves* were of variable composition. For example, he held that when an acid is added to an alkali, a continuous process of combination went on, the composition of the salt present in solution being determined by the relative amounts of acid and alkali present. He was well aware that if we take, *e.g.* a series of solutions obtained by mixing caustic soda solution and hydrochloric acid together in varying proportions, and evaporate them, the salt, sodium chloride, which we obtain always has a fixed composition; but he explained this by supposing that the compound of acid and alkali in this particular proportion was less soluble than a compound in any other proportion. Hence the mere fact that we obtain a salt of constant composition crystallising out from solution tells us nothing about the actual composition of the salt present *in* the solution. He applied a similar explanation to other compounds generally; and supported his views by pointing to some cases where compounds could be prepared which did appear to possess variable composition. For example:

1. Varying amounts of alkali added to solutions of certain metallic salts precipitated compounds containing varying proportions of acid and base. For example, excess of alkali added to boiling copper sulphate solution precipitated the black oxide; but by adding alkali insufficient to precipitate all the copper, and using cold solutions of copper sulphate, green precipitates were obtained, apparently containing varying amounts of acid still in combination with the copper.

2. Certain metals, such as tin and lead, seemed to be capable of combining with varying proportions of oxygen. Lead "forms an oxide which is grey, then passes through various shades of yellow, and finishes by being red," the amount of oxygen combining with the lead steadily increasing during these changes. Again, "the red oxide of mercury, when rubbed with mercury, divides its oxygen with an indefinite amount of the latter, and forms an oxide which . . . assumes various shades of greyish-yellow."

3. Aqueous solutions could be prepared containing the

dissolved substance in all proportions, up to a certain limiting value which depended on the temperature. The solution all the time remained perfectly homogeneous (that is, it showed no sign of containing more than one substance, one portion of solution being identical in all respects with any other portion). The same applied to certain metallic alloys of variable composition, and to many substances which, when fused together, formed homogeneous "glasses," which had "all the characteristics of a chemical combination, in that all the properties had become common."

Enough has been said to show that Berthollet had considerable grounds for attacking the statement that "substances always contain the same constituents in the same proportion by weight." There arose a controversy between him and Proust, which—to quote Thomson once more—"was carried on for some years with great spirit, but with perfect decorum and good manners on both sides." It ended with the victory of Proust. We must summarise drastically the vast amount of painstaking work which Proust did in order to verify his previous statement; it is hardly possible to do justice, in a couple of pages, to a discussion which lasted six years. The main points of Proust's arguments in support of the Law of Constant Proportions were the following:

1. Proust showed experimentally that the green precipitates obtained by adding alkali to copper sulphate solutions differed only from the black oxide of copper in that they contained water (*i.e.* were hydrated oxide of copper). The small and variable amounts of acid which they yielded on analysis were due merely to insufficient washing.

2. The apparently variable oxides of lead and of other metals were found to be mixtures of a definite oxide together with excess of metal; for example, on treating the greyish oxide of lead with very dilute nitric acid, or with acetic acid, a solution of ordinary lead nitrate or acetate was obtained, finely granulated lead separating during the process. Again, the yellowish oxide of mercury obtained by rubbing the red oxide with mercury was really a mixture of two oxides of

mercury; for, on treating this mixture with hydrochloric acid, calomel (insoluble mercurous chloride) and a solution of corrosive sublimate (mercuric chloride) were obtained. These chlorides were both of definite composition; and it is difficult to suppose that an original oxide of indefinite composition could have given this result, for, on treatment with acid, it would have had to decompose in such a manner as to give two oxides each containing just the right proportion of oxygen to form the respective chlorides. Proust remarked that "this is a case of oxides behaving with much intelligence."

3. In a vast number of cases, oxides and sulphides of metals can be shown to possess a definite composition, however the conditions of their preparation are varied. To take one example: 100 parts of antimony always give 135 to 136 parts of sulphide, whether the antimony were heated with excess of sulphur, or with excess of cinnabar (mercuric sulphide).

Antimony (volatile)	+	*sulphur* (volatile)	=	*antimony sulphide* (non-volatile)	+	*excess sulphur* (volatile)	
Antimony (volatile)	+	*cinnabar* (volatile)	=	*antimony sulphide* (non-volatile)	+	*mercury* (volatile)	+ *excess cinnabar* (volatile)

If 100 parts of antimony were weighed out, 135–136 parts of the non-volatile sulphide were left, after heating sufficiently to expel the volatile substance also present.

This, as has been stated, was only one of very many similar examples.

4. There still remained the solutions, alloys and glasses, which, it will be remembered, were perfectly homogeneous, but of variable composition. For example, the "compound" sugar contains carbon, together with hydrogen and oxygen, the latter elements being present in the same proportions as in water. In sugar the elements are "combined" chemically; in an aqueous solution of sugar, on the other hand, the water is not said to be so combined. What distinction can be drawn between the forces binding the carbon, hydrogen, and oxygen in sugar, and those which cause sugar to dissolve in water?

Proust, while giving no answer to this question, maintained that a clear distinction could be drawn in practice between

the effects of the two; that is to say, that a compound was clearly different from a solution, whatever might be the ultimate explanation of the difference. This view was very generally adopted, and we ourselves can leave it without further discussion; certain cases, such as "constant boiling mixtures," and "eutectic alloys," in which it is not always easy to distinguish between these mixtures and true compounds, will not affect the subject-matter of this book.

The controversy between Berthollet and Proust was useful in that it served to place on a secure basis the law which we have stated at the beginning of this chapter. Since then the truth of the law has been tested innumerable times, in the course of various analyses. For example, Stas, in determining the equivalent weights of silver and chlorine, prepared silver chloride in a variety of ways, obtaining the mean result:

1 part of silver combines with 0·32845 part of chlorine.

The extreme variation in the weights of chlorine combining with a constant weight of silver did not exceed 0·003 per cent.

Hence the law of constant proportions, together with that of the conservation of mass, form the foundation stones of modern chemistry; though the attitude towards these laws has changed somewhat of recent years.*

EXERCISES ON CHAPTER VI

The student who has mastered sufficient physical chemistry to understand the meaning of eutectic alloys, cryohydrates, and constant-boiling mixtures, will find it profitable to discuss the following question:

How far may fixity of composition be taken as a criterion of chemical combination?

* See pp. 55, 289.

CHAPTER VII

THE STUDY OF SALTS, AND THE LAW OF EQUIVALENTS, OR OF RECIPROCAL PROPORTIONS

THIS chapter will conclude our survey of the most important quantitative work which was done in chemistry up to the time of the appearance of Dalton's Theory. It takes us back, to begin with, a good many years.

Salts, to the early chemists, were " a class of bodies which were soluble in water, having taste, and resisting the action of fire " (Marsh, *The Origins and Growth of Chemical Science*). Salts differed from earths, the latter being also resistant to fire, but insoluble in water. It was Boyle who first clearly recognised that salts were formed by the combination of acid and alkali ; and some quantitative work on salt formation was done by Homberg, without, however, leading to any conclusions of great value. Bergman's *Tables of Affinity*, to which we referred in the last chapter, were qualitative in nature ; and the first important quantitative work on salts was done by Joseph Black (1728–1799), who published, in 1754, his dissertation entitled *Experiments upon Magnesia alba, quicklime, and other alkaline substances*. In this Black demonstrated clearly the existence of a substance which he called " fixed air," which was different from ordinary air, and which was fixed (hence the name) in limestone, magnesia, and similar substances, being liberated from them by the action of heat or of an acid. Black was able to show that the expulsion of the fixed air from an alkali, though it rendered that alkali caustic, had no effect upon

its neutralising power (since a given weight of chalk neutralised the same amount of acid, whether or not the chalk had first been heated to drive off the fixed air); he showed also that a given weight of chalk liberated the same weight of fixed air, whether it was merely heated, or whether it was treated with acid; and finally, that on heating a given weight of chalk until it was converted to quicklime, and treating the quicklime obtained with a solution of "fixed alkaline salt" (*i.e.* carbonate of sodium or potassium), a powder exactly resembling chalk was obtained, equal in weight to that originally taken. He concluded correctly that substances such as chalk and magnesia contained a caustic alkali combined with fixed air.

This work of Black's led to a concentration of interest upon the composition of salts; and in particular, Cavendish performed some important experiments upon the neutralisation of alkalis and acids. Cavendish introduced the word *equivalent* into chemistry, giving it a precise meaning. A given weight of potash, for example, was said to be equivalent to another weight of lime, when both neutralised the same weight of a given acid. These two weights, of potash and lime respectively, hence are "equal in value" with respect to neutralisation of an acid.

In 1788 Cavendish demonstrated that the use of equivalents could be extended; he studied, for example, the action of the two acids, nitric and sulphuric, upon the two bases, marble and potash. His results may be expressed as follows:

Let A = the weight of sulphuric acid neutralising X grams of marble.
B = the weight of nitric acid neutralising X grams of marble.
Y = the weight of potash neutralising A grams of sulphuric acid.

Then Y will also be the weight of potash neutralising B grams of nitric acid.

In other words, Cavendish " showed that the quantities of nitric and sulphuric acids which neutralise two identical weights of potash would also neutralise two identical weights of marble, different from those of the potash. This was the first clear recognition of equivalent weights of substances which interact chemically " (Partington, *Inorganic Chemistry*).

This important discovery was extended and generalised by Richter, who published, in 1792–1794, a treatise on *Stoichiometry*, *i.e.* the art of measuring the combining ratios of substances. In his numerical data, Richter seems to have been guilty of a certain amount of " adjustment," in order to fit an odd notion which he had that the equivalent weights of bases increased in an arithmetical progression, while those of acids increased in a geometrical progression. Nevertheless, the table of equivalent weights which he published was of considerable value. In it, the weights of a number of different bases are given, together with similar weights for acids. These weights are all equivalent ; that is to say, if the weight quoted of any base be mixed with the weight quoted of any acid, neutralisation results.

This general relationship between combining weights is not restricted to acids and bases ; it applies also to the combining weights of other compounds, and of elements. The law underlying this is usually called either the Law of Equivalents or the Law of Reciprocal Proportions. It may be expressed in various ways :

Substances unite only in the ratio of their combining weights (Ostwald).

The weights of two substances equivalent to the same weight of a third substance are equivalent to one another.

More fully :

If two substances, A and B, combine separately with a third substance, C, and also with one another, then the

weights of A and of B combining with a fixed weight of C will also be the relative weights of A and B which combine with one another.

This law is very generally used in finding the equivalent weights of elements by various methods. For example, suppose we define the equivalent weight of an element as that weight of it which combines with unit weight of hydrogen. It is evident that since all equivalent weights are fixed by the laws of Nature, it is only necessary to select a convenient unit, such as the above, in order to give them each a numerical value.

On the above definition the equivalent weight of chlorine is found to be 35·5, and that of oxygen, 8. Now, according to the Law of Equivalents, the equivalent weight, say, of a metal, will be that weight of the metal which will combine with (or displace) unit weight of hydrogen, *or* 35·5 units of chlorine, *or* 8 units of oxygen; for the same weight of the metal will do all these things. Hence, in determining the equivalent weight of the metal, we are at liberty to choose that reaction which is the easiest to carry out.

Strictly speaking, the Law of Equivalents should be stated in a more general form, in order to include the phenomena described in the Law of Multiple Proportions. Since, however, the latter law arose out of the Atomic Theory, and the former was developed quite independently of this theory, we will not deal with this for the present.

Exercises on Chapter VII

Illustrate the law of equivalents from the following examples:

1. A compound of carbon and hydrogen contains 75 per cent. carbon, 25 per cent. hydrogen by weight.
   An oxide of carbon contains 27·3 per cent. carbon.

Water contains 11·1 per cent. hydrogen, 88·9 per cent. oxygen.
A chloride of carbon contains 7·8 per cent. carbon.
An oxide of chlorine contains 18·4 per cent. oxygen.

2. Phosphine contains 91·2 per cent. phosphorus, 8·8 per cent. hydrogen.
A chloride of phosphorus contains 22·55 per cent. phosphorus.
Hydrogen chloride contains 2·74 per cent. hydrogen.
An oxide of phosphorus contains 43·6 per cent. oxygen.
Water contains 11·1 per cent. hydrogen, 88·9 per cent. oxygen.

PART III

THE ATOMIC THEORY OF JOHN DALTON

CHAPTER VIII

DALTON: HIS CONTRIBUTION TO CHEMISTRY

> " The invention all admired, and each how he
> To be the inventor missed ; so easy it seemed
> Once found, which yet unfound most would have thought
> Impossible."
>
> MILTON : *Paradise Lost.*

WE have seen in the preceding chapters that by the beginning of the nineteenth century the foundations of chemistry had been laid ; with the Laws of Conservation of Mass, and of Constant and Reciprocal Proportions, chemistry ceased to be purely qualitative, and became an exact science. These laws were, however, fundamentally empirical ; they corresponded exactly with the definition of a " law " given in Chap. I—that is, they were general statements, founded upon experimental observation, which described the way in which substances behaved. There was, as yet, no theory underlying them all, explaining why substances should behave in this manner. We owe such a theory to John Dalton.

During the great scientific activity which developed during the Renaissance and the period immediately following, the atomic theory of Democritus and the other " atomistic philosophers " of ancient times was not entirely overlooked. The theory had, of course, fallen

completely into the background during the Middle Ages, for these, as we have seen, were dominated by the spirit of Aristotle; and Aristotle had dismissed the atomic theory on various grounds. Galileo, however, was inclined to accept the atomic theory; and the general concepts of Democritus and Lucretius were revised and extended by Gassendi about the middle of the seventeenth century; by this time, much progress had been made in the sciences of mechanics and astronomy, and men were disposed to favour the idea of a Universe which consisted essentially of matter in motion. The "corpuscular theory" of matter was used by Boyle, Newton, and others to provide explanations of physical phenomena; long before Dalton's time, an explanation of Boyle's law was put forward on lines which were afterwards developed into the kinetic theory of gases. Boyle wrote a memoir entitled "Some Specimens of an attempt to make Chymical Experiments useful to illustrate the notions of the Corpuscular Philosophy." Newton, in a famous passage in his *Opticks*, expressed his views on the structure of matter as follows:

> "It seems probable to me that God in the beginning formed matter in solid, massy, hard, impenetrable moveable particles; . . . and that these primitive particles being solids, are incomparably harder than any porous bodies compounded of them; even so very hard, as never to wear or break in pieces: no ordinary power being able to divide what God himself made One, in the first creation."

He further points out that, if matter be composed of atoms, there is direct evidence that these atoms must be supposed incapable of wearing out; for otherwise "water and earth composed of old worn particles and fragments of particles, would not be of the same texture now, with water and earth composed of entire particles."

These quotations and references have been given, not only on account of their interest, but also because there

is no doubt that Dalton was greatly influenced by them. It is clear from the above that Dalton did not invent the atomic theory, and that he did not even revive it in modern times. This being so, it must make us all the more careful to see exactly what there was in "Dalton's Theory" which was new and original.

John Dalton was born in 1766. According to Whewell, "Mr. Dalton, at the time when he conceived his theory, was a teacher of mathematics at Manchester, in circumstances which might have been considered narrow, if he himself had been less simple in his manner of life, and less moderate in his worldly views." He was, in fact, a schoolmaster; but even schoolmasters sometimes have bright ideas, and Dalton had several. Most of the quotations from his works which follow are taken from his *New System of Chemical Philosophy*, published in 1808 (first volume) and 1810 (second volume); though many of the ideas expressed in them were conceived some years earlier.

The first portion of the *New System* is occupied principally with ingenious speculations and experiments on the nature of heat, and, in particular, with his views on the constitution of gases, vapours, and so forth, from the physical standpoint; the latter portion is more concerned with chemistry. It will be convenient for us to reverse this order, and to consider first the famous chapter "On Chemical Synthesis," which comes at the end of the first volume. Without altering the essentials of Dalton's argument, we shall modify slightly the exposition; also, to avoid confusing the reader, we shall introduce the word "molecule" in its modern sense, though this was not actually done until later; Dalton, and his immediate successors used expressions such as "compound atom," or simply "atom," in ways somewhat misleading to the present-day student.

Atoms, according to Dalton, had the following characteristics:

(*a*) *They are minute particles, which cannot be split up, destroyed, or created.*

(*b*) *All the atoms of the same element are identical in every respect. In particular, they all have exactly the same weight.*

(*c*) *Atoms of different elements have different properties; in particular, they differ from one another in weight.*

(All oxygen atoms, for example, weigh the same; but the weight of an oxygen atom is a *characteristic property* of the element oxygen, and is different from the weight of an atom of nitrogen, or of any other element.)

There is nothing entirely original in the above statements, except that Dalton was the first to lay stress upon the weight of an atom as being one of its most important properties.

(*d*) *When atoms combine, they do so in simple numerical proportions, forming molecules (which Dalton called "compound atoms").*

(*e*) *All the molecules of a given compound are exactly alike.*

These are the original and important features of Dalton's theory; their importance lies in the fact that Dalton was able to *deduce* a consequence from them which he could verify by experiment. Dalton's theory thus fulfils the requirements of a scientific hypothesis which we laid down in Chap. I of this book.

To see clearly how Dalton did this, we will quote his own words:

"If there are two bodies, A and B, which are disposed to combine, the following is the order in which the combinations may take place, beginning with the most simple, viz.:

1 atom of A + 1 atom of B = 1 atom of C, binary."

(For "atoms," on the right-hand side of these equations, read of course "molecules.")

1 atom of A + 2 atoms of B = 1 atom of D, ternary.
2 atoms of A + 1 atoms of B = 1 atom of E, ternary.

1 atom of A + 3 atoms of B = 1 atom of F, quaternary.
3 atoms of A + 1 atom of B = 1 atom of G, quaternary, etc.

If we write formulæ, in the modern way, to represent the molecules of these compounds, they would be:

Binary.	Ternary.	Quaternary.
AB	AB_2 and A_2B	AB_3 and A_3B

and so on. In the compound C, *all* the molecules would have the composition AB, and in the compound D, all the molecules would have the composition AB_2, and so forth.

Now, suppose two elements, A and B, are capable of forming *two* compounds. Dalton considered it probable, in such a case, that one of the compounds would be the simple binary one, the molecules of which consist of one atom of A united with one of B (formula AB); and that the other compound would probably be ternary, the molecules consisting either of one atom of A united with two of B, or of one atom of B united with two of A (formulæ AB_2 or A_2B, respectively).

Let us suppose that the second compound has the formula AB_2; and suppose we take a quantity of the compounds, AB and AB_2, *such that the weight of the element A is equal in both.* Then both quantities must contain equal numbers of atoms of A. It further follows that the total number of atoms of B present in these quantities of the respective compounds must be as 1 : 2. Hence, since all the atoms of B weigh the same, *the weights of B combined with a fixed weight of A should be exactly* 1 : 2 *in the binary and ternary compounds respectively.*

For the benefit of those who like dealing with symbols, this argument may be repeated as follows:

Let a = the weight of one atom of A.
Let b = the weight of one atom of B.

We take a quantity of the binary compound, AB, and a quantity of the ternary compound, AB_2, such that the weight of A is the same in both.

Let w = the weight of A present in both quantities.

Then the number of atoms of A present in both will be x, where

$$x = \frac{w}{a}.$$

The number of atoms of B combined with x atoms of A will be x in the binary compound, and $2x$ in the ternary; and the corresponding weights of B combined with the weight w of A will be

$$x \times b \text{ in the binary compound,}$$
$$2x \times b \text{ in the ternary compound.}$$

That is, the weights of B combined with a fixed weight of A should be exactly 1 : 2 in the binary and ternary compounds respectively.

The reader should study this argument very carefully until he is sure that he fully understands it, and can reproduce it for himself. It will be seen to rest essentially upon the following features of Dalton's theory:

The atoms of the elements have definite, characteristic weights;

Atoms combine in simple numerical proportions;

The "compound atoms," or molecules, of a given compound are all precisely alike.

In the second volume of the *New System*, Dalton points in many places to experimental data which confirm this deduction. On p. 76, he quotes Clement and Desormes' values for the percentage composition of the two oxides of carbon:

	Per cent. carbon.	Per cent. oxygen.
Carbonic oxide ..	.. 44	56
Carbonic acid ..	.. 28·1	71·9

If, in the second case, we calculate the weight of oxygen combining with 44 parts of carbon, we find it to be

112 parts. That is, if we take a fixed weight of carbon, the weights of oxygen combining with it in the two oxides are as 1 : 2.

Perhaps the most famous example is that of the gases carburetted hydrogen and olefiant gas (methane and ethylene). Dalton analysed these gases as follows :

Both gases, on sparking alone, are decomposed into carbon (which occupies negligible volume) and hydrogen.

Equal volumes of each gas gave equal volumes of hydrogen.

On sparking with a sufficient quantity of oxygen, both gases yield water and carbon dioxide.

Since it has been shown that equal volumes of each gas contain the same amount of hydrogen, equal volumes of each gas will require the same amount of oxygen to burn the hydrogen to water.

Dalton was able to show that, when equal volumes of the two gases were taken, the volumes of *extra* oxygen (required to burn the carbon to carbon dioxide) stood in the ratio of 1 : 2 for carburetted hydrogen and olefiant gas respectively ; and that the volumes of carbon dioxide produced were also as 1 : 2.

Hence, for these two hydrocarbons, taking the same amount of combined hydrogen in both cases, the amounts of carbon combined with this fixed amount of hydrogen are as 1 : 2 ; *or, taking a fixed amount of carbon, the amounts of hydrogen combined are as* 2 : 1, *in carburetted hydrogen and olefiant gas respectively.*

This was the signal achievement of Dalton's theory ; the thing which distinguished it from all the qualitative speculations concerning atoms which had been made from time to time for more than 2,000 years before him. The earlier " atomistic philosophy " had been little more than a series of plausible guesses, incapable of proof or disproof. *Dalton, from a few simple and definite postulates, was able, as we have seen, to deduce a consequence which he could put to the test of experiment ;* and experiment confirmed his deduction. The result

was the discovery of a new and hitherto unsuspected law, namely, the "Law of Multiple Proportions."

This law may be stated in a form more general than that which we considered in the preceding pages, since it is evident that the ratios of the weights of one element need not always be as 1 : 2 ; it is sufficient that they should be in a *simple* ratio, such as 1 : 2, 1 : 3, 2 : 3, and so forth. Further, Dalton held that the "compound atoms" or molecules of compounds, when they combined, did so also in simple numerical proportions ; a supposition which was fully confirmed experimentally. Hence the Law of Multiple Proportions may be stated in the general form :

> "*When two substances combine together to form more than one compound, the weights of one substance combining with a fixed weight of the other are in a simple numerical ratio.*"

It is hardly necessary to point out that the existence of this law provides very strong evidence that matter is atomic in structure, and not continuous. Imagine, for example, that we take a certain weight of a metal such as barium, and oxidise it, first to barium oxide, and secondly to barium peroxide. The oxidation takes place in two definite stages, or "jumps" :

$$\text{Barium} + \text{oxygen} = \text{barium oxide}$$
$$\text{Barium oxide} + \text{oxygen} = \text{barium peroxide}$$

the oxygen being added in two exactly equal amounts. The atomic theory beautifully explains this by supposing that each atom of barium takes up first one oxygen atom and then another one ; and it is difficult to imagine any other theory which can account for such facts so simply and satisfactorily.

The atomic theory, as conceived by Dalton, is of course irreconcilable with Berthollet's view of the variable composition of chemical compounds, as Dalton himself

pointed out; but as this view was shown to be wrong by Proust, on evidence quite independent of the atomic theory, it is unnecessary to deal with this further. It is evident that the theory as it stood was capable of explaining satisfactorily the Laws of Conservation of Mass and of Constant Proportions.

Dalton's theory had an instantaneous success. Thomson, in his usual graphic way, describes how a number of eminent contemporary chemists were convinced, by virtue of the discovery of the law of multiple proportions, of its fundamental truth. Later, Dalton was honoured by being made a corresponding member of the Institute of France; he was presented with a medal by the Royal Society in 1826; and "in 1833, at the meeting of the British Association for the Advancement of Science, which was held in Cambridge, it was announced that the King had bestowed on him a pension of *l*150; at the preceding meeting at Oxford, that university had conferred upon him the degree of Doctor of Laws, a step the more remarkable, since he belonged to the sect of Quakers" (Whewell).

We have considered up till now those portions of Dalton's theory which were successful, and which the passage of time has confirmed in their essentials; but not all his views proved to be correct, as we shall see in the next few pages.

DALTON'S MISTAKES

"*Atomic Weights.*"—Dalton, as we have seen, was the first to lay stress upon the importance of the weights of atoms; and one of his main objects was to try to determine the relative weights of atoms of different elements. He realised, of course, that the actual weights of single atoms would be excessively small, and that his chemical experiments did not provide him with the data necessary for determining them; but for the purpose

of assigning formulæ to compounds it is only necessary to know the proportions by weight in which the elements composing the compound are present, together with the *relative* weights of the elementary atoms. If, then, we divide the weight of each element present by the relative weight of the corresponding atom, we obtain the proportions by atoms in which the elements are present, and hence can work out the empirical formula.*

It is necessary to select first a convenient unit in which to measure the relative weights of atoms; and Dalton naturally chose the weight of a hydrogen atom as his unit, this being the lightest known atom. The "atomic weight" of any element is then defined by the ratio

$$\frac{\text{weight of an atom of the element}}{\text{weight of an atom of hydrogen}}.$$

The atomic weight of hydrogen is of course 1, and that of any other element is greater that 1.

How can we find the relative weights of the atoms? Let us turn back for the moment to Dalton's examples of the Law of Multiple Proportions: the oxides of carbon, and the two hydrocarbons. It is shown that, taking a fixed weight of carbon, the weights of oxygen combined with it are as 1 : 2 in carbonic oxide and carbonic acid respectively, and the weights of hydrogen also as 1 : 2 in olefiant gas and carburetted hydrogen (marsh gas) respectively. This leads to the following conclusion regarding the molecules of these compounds:

$$\frac{\text{Number of oxygen atoms combined with 1 atom of carbon in carbonic acid}}{\text{Ditto in carbonic oxide}} = \frac{2}{1}$$

and

$$\frac{\text{Number of hydrogen atoms combined with 1 atom of carbon in marsh gas}}{\text{Ditto in olefiant gas}} = \frac{2}{1}$$

* See p. 207.

But the evidence in itself tells us nothing further. The oxides might have the following formulæ :

Carbonic oxide	..	CO	CO_2	CO_3	C_2O_3
		or	or	or	etc. ;
Carbonic acid	..	CO_2	CO_4	CO_6	CO_3

all of which satisfy the conditions that the proportions of oxygen combined with a fixed amount of carbon are as 1 : 2.

The same can be said of the hydrocarbons. For the two oxides we can write the general formulæ C_xO_y and C_xO_{2y} ; and for the two hydrocarbons C_xH_y and C_xH_{2y}. We are justified in assuming that x and y are probably *small* whole numbers (since, if atoms did not combine in *simple* ratios the law of multiple proportions would not hold good) ; but we cannot, without further evidence, ascertain what these numbers really are. In particular, we are not justified in assuming that x and y are both equal to 1.

But this was just what Dalton did. In the chapter " On Chemical Synthesis " he laid down the following rules :

" 1st. When only one combination of two bodies can be obtained " (*i.e.* when two elements form only *one* compound), " it must be presumed to be a *binary* one unless some cause appear to the contrary.

" 2nd. When two combinations are observed, they must be presumed to be a binary and a ternary.

" 3rd. When three combinations are obtained, we may expect one to be a binary, and the other two ternary."

And so forth. The gist of all this is really the following :

The existence of the law of multiple proportions shows that atoms combine in small whole numbers. Very well ; we will go further, and assume that they combine in the simplest possible way. When two elements form only one compound, we will assume, unless something turns up to indicate other-

wise, that the ratio of atoms in the compound is 1 : 1; if two compounds are formed, that the ratios are 1 : 1 and 1 : 2, if three, 1 : 1, 1 : 2, and 2 : 1, and so on.

On the strength of this, Dalton wrote the formulæ for the two oxides of carbon CO and CO_2 (carbonic oxide and carbonic acid), and for the two hydrocarbons CH and CH_2 (olefiant gas and marsh gas). We know now that his reasoning was unsound; he happened to be right in the case of the oxides, but wrong in that of the hydrocarbons; the formulæ of olefiant gas and marsh gas are C_2H_4 (giving the *empirical* formula CH_2) and CH_4 respectively.

Dalton further drew up a table of atomic weights; it is interesting to compare these weights with the modern values.

	Atomic Weight (Dalton).	Atomic Weight (H = 1) (1921).
Hydrogen	1	1
Oxygen	7	15·87
Azote	5	13·9
Carbon	5·4	11·9
Sulphur	13	31·8
Phosphorus	9	30·8
Silver	100	107
Zinc	56	64·85

The mistakes in this table arise from two sources:

(*a*) inaccurate analyses, giving fractional errors in the atomic weights (for example, giving the atomic weight of silver as 100 instead of 107).

(*b*) incorrect formulæ. This gives values which have to be multiplied by a whole number to give the correct value.

For example, following his general rule, Dalton wrote the formula for water (the only known compound of hydrogen and oxygen) as HO. Even assuming accurate analysis, this would have given 7·98 as the atomic weight of oxygen, which is half the correct value.

Again, writing the formula for marsh gas CH_2 instead of

CH_4 halves the atomic weight of carbon, giving, instead of 11·9, the value 5·95 (Dalton's figure being 5·4).

Enough has been said to show that Dalton's "rules of combination" were not only unjustifiable guesses, but that they led him astray regarding the atomic weights of most of the common elements. The correct method of solving the problem of atomic weight determinations was found later to lie in the study of gases; but by a curious irony Dalton rejected the evidence which would have guided him on to the right path.

Before considering briefly his views on gases, we might mention that Dalton himself admits here and there that his rules were somewhat uncertain, as in the following passage:

"After all, it must be allowed to be possible that water may be a ternary compound. In this case, if two atoms of hydrogen unite to one of oxygen, then an atom of oxygen must weigh 14 times as much as one of hydrogen; if two atoms of oxygen unite to one of hydrogen, then an atom oı oxygen must weigh 3½ times one of hydrogen."

Dalton's Picture of a Gas.—One of the principal differences between a gas on the one hand, and a solid or liquid on the other, is that the former will expand freely to fill any space in which it is confined, and may be compressed into a small volume; whereas solids and liquids require relatively enormous forces to produce any sensible alteration of volume.

If gases are composed of atoms, we must suppose, in order to account for this expansibility and compressibility, either that the atoms themselves can be expanded or compressed to very great extents, or that they are separated in a gas by spaces which are large compared with the actual size of the atoms. The former seems very unlikely; but if we accept the latter as more probable, we have to account in some way for the fact that the atoms keep apart from one another, and do not merely fall to the

bottom of the vessel under the influence of gravity. There are two possible ways of doing this. In the first place, we may suppose that the atoms are in a continual state of rapid motion, keeping apart by virtue of the collisions which they make with one another, and with the walls of the vessel. In the second, we may suppose them stationary, but separated from one another by some repulsive force.

The former is the view adopted in the modern " kinetic theory of gases "; the latter was that taken by Dalton. In notes written for a lecture delivered at the Royal Institution in 1810, he says :

> " Newton had demonstrated clearly in the 23rd Prop. of Book II of the *Principia* that an elastic fluid " (a gas) " is constituted of small particles or atoms of matter which repel each other by a force increasing in proportion as their distance diminishes."

In the *New System*, he writes as follows :

> " A vessel full of any pure elastic fluid presents to the imagination a picture like one full of small shot. The globules are all of the same size ; but the particles of the fluid differ from those of the shot, in that they are constituted of an exceedingly small central atom of solid matter, which is surrounded by an atmosphere of heat, of great density next the atom, but gradually growing rarer according to some power of the distance."

At the time when Dalton wrote, heat was considered to be some kind of material fluid ; it was not until later that the experiments of Rumford and others showed it to be a form of motion.

Some further observations on the combination of gases are of great importance. Dalton states that at one time he had " a confused idea " that

> " the particles of elastic fluids are all of the same size ; that a given volume of oxygenous gas contains just as many particles as the same volume of hydrogenous gas ; or if not, that we had no data from which the question could be solved."

In other words, Dalton imagined at one time that equal volumes of gases, at the same temperature and pressure, contained equal numbers of particles. Had he been able to develop this idea into the conception we now know as Avogadro's hypothesis, the progress of chemistry might have been accelerated by some fifty years. Unfortunately, however, he proceeds :

> " But from a train of reasoning . . . I became convinced that different gases have *not* their particles of the same size : and the following may be adopted as a maxim, till some reason appears to the contrary : namely :
>
> " That every species of pure elastic fluid has its particles globular and all of a size, but that no two species agree in the size of their particles, the pressure and temperature being the same."

From this, of course, it would follow that equal volumes of gases, at the same temperature and pressure, do *not* contain equal numbers of particles.

It is interesting to see the reasons on which Dalton based this conclusion. He refers to p. 71 of his book, where we find some reflections upon nitrous gas (now known as nitric oxide). Davy, about 1800, repeating an earlier experiment of Priestley's, had burnt charcoal in the gas, by applying a burning-glass to the charcoal for about four hours. Under these conditions, the nitric oxide is decomposed, giving nitrogen and carbon dioxide.

Davy found that 15·4 volumes of nitric oxide gave 7·4 volumes of nitrogen and 8·7 volumes of carbon dioxide. It was known that carbon burns in oxygen without change of volume ; *i.e.* that one volume of carbon dioxide " contains " one volume of oxygen. Hence the result is obtained that

15·4 volumes of nitric oxide contain 7·4 volumes of nitrogen
and
8·7 volumes of oxygen.

Suppose *for the moment* that we assume that

2 volumes of nitric oxide contain 1 volume of nitrogen
and
1 volume of oxygen,

the deviations from this simple ratio being due to experimental errors. Suppose, further, that we assume that "the particles of elastic fluids are all of the same size"; that is, in particular, that 1 volume of nitric oxide, 1 volume of nitrogen, and 1 volume of oxygen, all contain the same number of ultimate particles of nitric oxide, nitrogen, and oxygen respectively; and suppose this number to be x. The above experimental result would therefore lead to the conclusion that

$$\left.\begin{array}{c}2x \text{ particles of} \\ \text{nitric oxide}\end{array}\right\} \text{ are obtained from } \left\{\begin{array}{c}x \text{ particles of nitrogen} \\ \text{and} \\ x \text{ particles of oxygen.}\end{array}\right.$$

This conclusion seemed to Dalton to run counter to the whole principle of the atomic theory. For, even if we give nitric oxide the simplest possible formula, namely NO, it must require 1 atom of nitrogen *and* 1 atom of oxygen to produce 1 molecule of nitric oxide. *Dalton, in common with all contemporary chemists prior to Avogadro, naturally imagined that the "ultimate particles" of elementary gases consisted of single atoms;* hence it did not seem possible that x ultimate particles of nitrogen and x of oxygen could give more than x ultimate particles of nitric oxide, which means that 1 volume of nitrogen and 1 of oxygen could not give more than 1 volume of nitric oxide. It was, of course, Avogadro who supplied the solution; but Dalton, faced with the apparent contradiction, decided that the whole argument was fallacious; that equal volumes of gases did not contain equal numbers of particles, and that therefore there was probably no simple relationship between the combining volumes of gases. In his own words:

"No two elastic fluids, probably, therefore, have the same number of particles, either in the same volume or the same weight."

This erroneous conclusion will be referred to again (see next chapter) ; meanwhile it is well worth while reading through Dalton's argument carefully, to see how natural his mistake really was.

References

Dalton : *A New System of Chemical Philosophy.*

Alembic Club Reprints, No. 2 : *Foundations of the Atomic Theory.* Comprising Papers and Extracts by John Dalton, William Hyde Wollaston, M.D., and Thomas Thomson, M.D., 1802–1808.

Thomas Thomson : *A History of Chemistry.*

(In this history—a most delightful book—Thomson states that Dalton was led to the atomic theory as a result of the discovery of the Law of Multiple Proportions, whereas the opposite seems to have been the case ; *cf.* Roscoe and Harden, *A New View of the Origin of Dalton's Atomic Theory*, 1896.)

If the reader has access to Whewell's *History of Scientific Ideas*, he will find, in Book VI, Chap. V, some reflections on the atomic theory which, though superseded by later knowledge, are very interesting. It is a good exercise to read through this chapter, and meet the various objections which Whewell urges to the theory.

Exercises on Chapter VIII

1. State clearly the fundamental postulates of Dalton's theory, and show how the Law of Multiple Proportions follows from them.

2. Explain the Law of Equivalents on the basis of Dalton's theory. How should the simple statement of this law, given on p. 67, be modified so as to embrace the Law of Multiple Proportions ?

3. Two chlorides of a certain metal contain 55·94 and 65·58 per cent. of chlorine respectively.

Show that these compounds obey the Law of Multiple Proportions.

4. The percentages of nitrogen in its five oxides are respectively 63·65, 46·69, 36·86, 30·45 and 25·94.

Calculate the weights of oxygen combining with unit weight of nitrogen in each oxide, and show that the results illustrate the Law of Multiple Proportions.

5. Two carbonates, A and B, of a certain metal gave the following results on analysis :

(*a*) 0·426 grm. of A was dissolved in 100 c.c. of water. 10 c.c. of the solution neutralised 8·04 c.c. N/10 HCl.
(*b*) 0·649 grm. of B was dissolved in 100 c.c. of water. 10 c.c. of the solution neutralised 7·73 c.c. N/10 HCl.
(*c*) 1·00 grm. of A, on treatment with excess of concentrated sulphuric acid, liberated 0·415 grm. of carbon dioxide.
(*d*) 1·00 grm. of B, similarly treated, liberated 0·524 grm. of carbon dioxide.

Show that these results may be used to illustrate the Law of Multiple Proportions.

(Hint : regard the carbonates as compounds of base with carbon dioxide ; and show that the weights of carbon dioxide combined with a fixed amount of base are in a simple ratio.)

6. 0·613 gram of a certain metal, dissolved in concentrated hydrochloric acid, liberated 126 c.c. of hydrogen, collected over water at 15° C. and 748 mm.

0·416 grm. of the same metal was converted into oxide by treatment with concentrated nitric acid. 0·528 grm. of the oxide was obtained.

Show, with the help of the Law of Equivalents, that these results illustrate the Law of Multiple Proportions.

(Pressure of water vapour at 15° C = 13 mm.)

PART IV

THE STUDY OF GASES AND ITS APPLICATION TO THE DETERMINATION OF ATOMIC WEIGHTS

INTRODUCTION

THE solution to Dalton's difficulty was forthcoming only a few years later. In 1808 Gay-Lussac suggested that gases combine in simple proportions by volume; in 1811 Avogadro put forward his famous hypothesis; and it was shown later by Cannizzaro that this hypothesis afforded a means of determining atomic weights of many elements on a sound theoretical basis. But the gap between Avogadro and Cannizzaro was about fifty years! It seems astonishing to us now that the method developed by Cannizzaro was not discovered earlier; but the long delay, during which theoretical chemistry fell nearly into chaos, was due to several reasons. One was that Dalton, as we shall see, roundly declared that Gay-Lussac's law was a delusion; hence Avogadro's hypothesis, which was based on it, must be doubly a delusion. Dalton's influence among chemists was very great; and though many of the leading chemists of the time were by no means satisfied with his arbitrary rules regarding the combination of atoms together, it was partly due to Dalton that Avogadro's paper failed to attract the attention it deserved. Again, Cannizzaro's method is applicable only to substances which are either gaseous at ordinary temperatures, or which can be

vaporised without decomposition of their molecules ; and the number of such substances known at the beginning of the nineteenth century was comparatively limited.

As we have said, from 1810 to 1860 chemists got terribly muddled in their attempts to determine atomic weights, for lack of a really sound theory on which to base their results. If we were to treat of atomic weight determinations in strict chronological order, there would be a danger that the reader's mind would become equally muddled. Fortunately, though twentieth-century scientists make plenty of muddles of their own, with regard to atomic weights we can be "wise after the event," and pass straight from Avogadro's hypothesis to Cannizzaro's method, following thereby a logical sequence. From that, we can return to a consideration of the results gained in other directions during the first half of the nineteenth century without fear of repeating old mistakes. The story of this part of chemistry shows, as plainly as possible, that if knowledge is to be gained, theory and observation must go hand in hand ; and it provides a crushing answer (if any were necessary in these days) to those ignorant persons who declare that "Science is just a collection of facts."

CHAPTER IX

GAY-LUSSAC'S LAW OF GASEOUS COMBINATION

THE year 1808 saw, besides the appearance of Dalton's *New System of Chemical Philosophy*, the publication of a paper by the French chemist, Gay-Lussac, on the combination of gases. Three years previously Gay-Lussac had investigated the combination of hydrogen and oxygen by volume (an experiment first done by Cavendish), and from his results, corrected for some impurities in the gases, had calculated that 100 volumes of pure oxygen should combine with 199·89 volumes of pure hydrogen, or 200 volumes of hydrogen, within the limits of error of the experiment. This simple relationship of 2 volumes of hydrogen to 1 of oxygen made an impression on his mind, and he resolved to see whether equally simple relationships were found in other cases. His researches, which are summarised below, led him to conclude that they were.

His paper of 1808 begins with a few general reflections upon solids, liquids, and gases. He pointed out that solids and liquids expand to different extents when heated, and that their volumes are likewise altered differently when they are subjected to the same compressing force. All gases, on the other hand, expand equally when heated at constant pressure, and contract equally when compressed at constant temperature. Gases thus obey "simple and regular laws" with respect to temperature and pressure, while solids and liquids show more complicated behaviour.

Gay-Lussac explained this difference by supposing that the molecules of solids and liquids are held together by

cohesive forces (forces of attraction); this accounts for the fact that every solid and every liquid behaves differently from every other when heated or compressed. In gases, however, the individual particles are so far apart that the effect of cohesion is negligible.

He then proceeds to show that the simplicity exhibited by gases with respect to their physical behaviour extends to their chemical behaviour, and quotes a number of cases in which gases combine in simple proportions by volume (the gases, of course, being measured under the same temperature and pressure; this will be assumed in what follows). His examples include the following:

Ammonia and carbon dioxide:

200 volumes of ammonia combine with 100 vols. of carbon dioxide.

Composition of sulphuric acid (*i.e. sulphur trioxide*)*:*

100 vols. sulphurous gas + 50 vols. oxygen.

Composition of ammonia (calculated from the density of the gas, and also by sparking it):

100 vols. nitrogen + 300 vols. of hydrogen.

The oxides of carbon:

100 vols. carbonic oxide + 50 vols. oxygen give
100 vols. carbonic acid gas.

The oxides of nitrogen:

The percentage compositions *by weight* of three of the oxides of nitrogen were known. Gay-Lussac ingeniously points out that if we divide these percentages by the respective densities of the gases, we shall obtain the proportions by volume in which the gases would unite. The following are the figures quoted by him:

"Davy, from the analysis of various compounds of nitrogen with oxygen, has found the following proportions by weight:

	Nitrogen.	Oxygen.
Nitrous oxide	63·30	36·70
Nitrous gas*	44·05	55·95
Nitric acid †	29·50	70·50

* Nitric oxide † Nitrogen peroxide.

Reducing these proportions to volumes, we find :

	Nitrogen.	Oxygen.
Nitrous oxide	100	49·5
Nitrous gas	100	108·9
Nitric acid	100	204·7 "

Gay-Lussac considered that these volumes of oxygen only differed from 50, 100, and 200 respectively by amounts within the limits of experimental error. The greatest deviation from the round number is in the case of nitrous gas ; and he performed an analysis of this gas which satisfied him that the proportions of nitrogen and oxygen by volume contained in it were equal. This experiment was the following :

"On burning the new combustible substance from potash" (potassium metal, obtained the year before by Davy, who passed an electric current through fused potassium hydroxide) " in 100 parts by volume of nitrous gas, there remained over exactly 50 parts of nitrogen."

This showed that nitrous gas contains half its volume of nitrogen ; further, by subtracting the weight of nitrogen from the weight of nitrous gas, the weight of oxygen present was obtained ; and this weight could be divided as before by the density of oxygen to give the volume. The results showed

" that this gas is composed of equal parts by volume of nitrogen and oxygen.

" We may therefore admit the following numbers for the proportions by volume of the compounds of nitrogen with oxygen :

	Nitrogen.	Oxygen.
Nitrous oxide	100	50
Nitrous gas	100	100
Nitric acid	100	200

" . . . Thus it appears evident to me that gases always combine in the simplest proportions when they react with one another ; and we have seen in reality in all the preceding examples that the ratio of combination is 1 to 1, 1 to 2, or 1 to 3."

This simple proportionality by volume also extends to the

product of combination of the gases, if this be also a gas ; thus it appears from the above that

2 vols. of carbon monoxide + 1 vol. of oxygen give 2 vols. of carbon dioxide ;
1 vol. of nitrogen + 1 vol. of oxygen give 2 vols. of nitric oxide ;

and it was shown further that

2 vols. of hydrogen + 1 vol. of oxygen give (if measured at a temperature above 100° C.) 2 vols. of steam.

Hence we may state Gay-Lussac's law as follows :

Gases combine in simple proportions by volume ; and the volume of the product, if gaseous, also bears a simple relationship to the volumes of the combining gases. All volumes must be measured at the same temperature and pressure.

DALTON'S CRITICISM

What were Dalton's views on Gay-Lussac's memoir ? It may be as well to repeat briefly the conclusions to which he had already come. Two essential points of his theory, it will be remembered, were—

(*a*) Atoms cannot be split up ;
(*b*) Atoms combine in simple numerical proportions (1, 1 : 2, 1 : 3, etc.).

He had argued, in the *New System*, that one atom of nitrogen and one of oxygen could not produce more than one " compound atom " (molecule) of nitrous gas (nitric oxide). Hence he had rejected his first " confused idea " that equal volumes of gases, at a given temperature and pressure, contained equal numbers of particles, since, if this were so, one volume of nitrogen and one of oxygen could not give more than one volume of nitrous gas. Actually, however, they give " nearly two." If, then, we were to cling to the notion that equal volumes of gases contain equal numbers of particles, we should have to

suppose that the atoms of nitrogen and oxygen could split up into two parts, which shatters the very foundation of the atomic theory.* Dalton therefore concluded that the space occupied by an ultimate particle of a gas depends on the particular gas, having a characteristic value for that gas, just as the weights of atoms are characteristic of a particular element.

Dalton, therefore, was not favourably disposed towards the results published by Gay-Lussac ; and he dealt with them rather scornfully in the Appendix to the second volume of the *New System.*

> " His (Gay-Lussac's) notion of measures is analogous to mine of atoms."

That is, Dalton had said that atoms combine in simple ratios, while Gay-Lussac maintained that the volumes of gases combining were in simple ratios. He went on to remark that

> " if it could be proved that all elastic fluids have the same number of atoms in the same volume, or numbers that are as 1, 2, 3, etc., the two hypotheses would be the same, except that mine is universal, and his applies only to elastic fluids. Gay-Lussac could not but see . . . that a similar hypothesis had been entertained by me, and abandoned as untenable ; however, as he has revived the notion, I shall make a few observations upon it, though I do not doubt but he will soon see its inadequacy."

There followed a declaration that, according to the most accurate experiments, the proportions by volume in which gases combined were not really simple. Regarding the experiment of Gay-Lussac's, in which he burnt potassium in nitric oxide, obtaining 50 volumes of nitrogen from 100 of the oxide, he commented :

> " The degree of purity of the nitrous gas, and the particulars of the experiment, are not mentioned. This one result

* This is fully considered in the next chapter.

is to stand against the mean of three experiments of Davy, and may or may not be more correct, as hereafter shall appear."

It is fairly obvious what Dalton thought of the "one result"!

Finally:

"The truth is, I believe, that gases do not unite in equal or exact measures in any one instance; when they appear to do so, it is owing to the inaccuracy of our experiments. In no case, perhaps, is there a nearer approach to mathematical exactness than in that of 1 measure of oxygen to 2 of hydrogen; but here, the most exact experiments I have ever made gave 1·97 hydrogen to 1 oxygen."

Dalton, then, was firmly opposed to Gay-Lussac's law at the time when it was put forward; and he remained so. We shall consider this further in Chapter XII.

In conclusion, it may be emphasised that Gay-Lussac was concerned merely with the statement of an experimental *law*. Though this law was questioned at the time, it has since been confirmed in very many instances. It is a general statement describing the behaviour of gases. The next chapter will deal with the *hypothesis* which was put forward to explain this behaviour; though there is by now almost overwhelming evidence that this hypothesis is correct, it must not be overlooked that it stands essentially upon a different footing from the law of Gay-Lussac. Whatever view of the constitution of matter may be adopted by contemporary science, it must be capable of explaining Boyle's, Charles', and Gay-Lussac's laws; it is conceivable that different theories might be found to explain the laws, but the laws themselves remain unalterable.

CHAPTER X

AVOGADRO'S HYPOTHESIS

"M. Gay-Lussac has shown in an interesting memoir . . . that gases always unite in a very simple proportion by volume, and that when the result of the union is a gas, its volume also is very simply related to those of its components. . . . The first hypothesis to present itself in this connection, and apparently even the only admissible one, is that the number of integral molecules in any gases is always the same for equal volumes."—AMADEO AVOGADRO, *Journal de Physique*, 1811.

As a perfect understanding of Avogadro's hypothesis is essential if the reader is to follow the rest of this book intelligently, his argument will be put as clearly as possible, and not in his original words, which are sometimes involved. We may begin by removing a possible source of difficulty in the reader's mind.

The Nature of a Gas.—The reader probably knows already that Avogadro's hypothesis states that "equal volumes of all gases, at the same temperature and pressure, contain equal numbers of molecules." This is sometimes misunderstood to mean that the molecules of all gases are the same size, which is of course absurd. We do not believe that a molecule of steam, for example, which contains two atoms of hydrogen combined with one atom of oxygen, is no bigger than a molecule of hydrogen, which contains only two atoms of hydrogen. The actual volume of the molecule of steam itself is presumably about equal to that of two atoms of hydrogen + that of one atom of oxygen. In a gas, however, the molecules are separated by distances which, though small in themselves, are large compared with the dimensions of the

individual molecule. In oxygen gas at normal temperature and pressure, for example, it has been calculated that the average distance * between one oxygen molecule and another is about 3×10^{-7} cm., while the diameter of an individual oxygen molecule is about 3×10^{-8} cm. Hence the distance between one molecule and another is roughly ten times the diameter of a single molecule—if we imagine the oxygen molecules magnified to the size of a football, the distances between them would be more than three yards. These figures were not known, of course, until long after the time of which we are speaking; but they may serve to show how we can imagine equal volumes of different gases containing equal numbers of molecules, although the molecules may be of different sizes.

We have already referred (p. 83) to the query as to how it is that these molecules remain separated, and do not simply fall down under the action of gravity. Dalton imagined that they were stationary, being separated by an "atmosphere of heat." We no longer hold this view; but for the present it will be just as well if the reader imagines that the molecules *are* stationary, being kept apart by some force of repulsion. Once he has grasped Avogadro's hypothesis, he will have no difficulty in enlarging his mental picture to fit the modern conception of a gas.

Avogadro's Theory.—We must now ask the reader to forget, if he can, that he has ever been told anything about Avogadro, and to imagine that he is living about the year 1810; also, that he regards Gay-Lussac's law as true. In the following argument we shall use the word "molecule" to denote "ultimate particle" of *any* gas, whether the gas is an element or a compound. We shall also naturally assume, until evidence arises to disprove it, that the ultimate particles, or molecules, of the elementary gases, such as oxygen, hydrogen, and nitrogen, consist of single atoms.

* Not to be confused with the "mean free path."

According to Dalton's theory,

ATOMS COMBINE IN SIMPLE NUMERICAL PROPORTIONS TO FORM MOLECULES; AND MOLECULES OF COMPOUNDS ALSO COMBINE IN SIMPLE NUMERICAL PROPORTIONS AMONG THEMSELVES.

Gay-Lussac had shown that

GASES COMBINE IN SIMPLE PROPORTIONS BY VOLUME; and that THE VOLUME OF THE PRODUCT, IF A GAS, ALSO BEARS A SIMPLE RELATION TO THE VOLUMES OF THE COMBINING GASES.

For example, Dalton had shown (see p. 76) that

In the two oxides of carbon, the weights of oxygen combined with a fixed weight of carbon were as 1 *to* 2.

He therefore wrote the formulæ of the two oxides as CO and CO_2 respectively, and the equation for the formation of the higher oxide from the lower became

$$CO + O = CO_2.$$

Hence *one molecule of carbon monoxide produces one molecule of carbon dioxide.*

But we also have the experimental fact that

One volume of carbon monoxide produces one volume of carbon dioxide.

Now, since

1 molecule of carbon monoxide produces one molecule of carbon dioxide,
x molecules of carbon monoxide produce x molecules of carbon dioxide (where x is any whole number).

So we have the following parallel statements—

1 volume of carbon monoxide produces 1 volume of carbon dioxide (experimental fact);

x molecules of carbon monoxide produce x molecules of carbon dioxide (according to Dalton's Theory).

Therefore

if 1 volume of carbon monoxide contains x molecules, then 1 volume of carbon dioxide will also contain x molecules.

That is,

EQUAL VOLUMES OF CARBON MONOXIDE AND CARBON DIOXIDE CONTAIN EQUAL NUMBERS OF MOLECULES.

But Dalton's theory, and Gay-Lussac's law, apply to *any* molecules, and *any* gases; so we reach the general conclusion:

EQUAL VOLUMES OF ALL GASES (UNDER THE SAME CONDITIONS OF TEMPERATURE AND PRESSURE) CONTAIN EQUAL NUMBERS OF MOLECULES.

The Difficulty.—There is (or was, in the time of Dalton) a difficulty. We have seen, in the case of the oxides of carbon, that we are driven to the conclusion that equal volumes of these gases, at the same temperature and pressure, contain equal numbers of molecules. But if this be true of these two gases, it must also be true of the oxygen gas; it is illogical to grant the equality to two of the gases, and to deny it to the third.

It must be remembered that we are supposing that the ultimate particles, or molecules, of carbon monoxide, carbon dioxide, and oxygen have the composition CO, CO_2 and O respectively; in *particular, that the molecules of oxygen consist of single atoms.*

Now let us return to Dalton's equation for the combustion of carbon monoxide:

$$CO + O = CO_2$$

Since, according to this equation,

$$\left.\begin{array}{c}\text{1 mol. of carbon}\\\text{monoxide}\end{array}\right\}\text{ unites with }\left\{\begin{array}{c}\text{1 mol. of}\\\text{oxygen}\end{array}\right\}\text{ to give }\left\{\begin{array}{l}\text{1 mol.}\\\text{of carbon}\\\text{dioxide,}\end{array}\right.$$

$$\left.\begin{array}{c}x\text{ mols. of carbon}\\\text{monoxide}\end{array}\right\}\text{ unite with }\left\{\begin{array}{c}x\text{ mols of}\\\text{oxygen}\end{array}\right\}\text{ to give }\left\{\begin{array}{l}x\text{ mols.}\\\text{of carbon}\\\text{dioxide.}\end{array}\right.$$

If, then, equal volumes of all three gases contain equal numbers of molecules, x molecules of carbon monoxide, x molecules of oxygen, and x molecules of carbon dioxide should all occupy the same volume ; and we should obtain that

$$\left.\begin{array}{c}\text{1 volume of carbon}\\\text{monoxide}\end{array}\right\}\begin{array}{c}\text{unites}\\\text{with}\end{array}\left\{\begin{array}{c}\text{1 volume of}\\\text{oxygen}\end{array}\right\}\text{ to give }\left\{\begin{array}{l}\text{1 volume}\\\text{of carbon}\\\text{dioxide.}\end{array}\right.$$

But this is not what we actually do find. Actually we find that

$$\left.\begin{array}{c}\text{1 volume of carbon}\\\text{monoxide}\end{array}\right\}\begin{array}{c}\text{unites}\\\text{with}\end{array}\left\{\begin{array}{c}\text{HALF A VOLUME}\\\text{OF OXYGEN}\end{array}\right\}\begin{array}{c}\text{to}\\\text{give}\end{array}\left\{\begin{array}{l}\text{1 volume}\\\text{of carbon}\\\text{dioxide ;}\end{array}\right.$$

which leads to the conclusion that

$$\left.\begin{array}{c}x\text{ mols. of carbon}\\\text{monoxide}\end{array}\right\}\text{unite with}\left\{\begin{array}{c}\frac{x}{2}\text{ mols. of}\\\text{oxygen}\end{array}\right\}\text{ to give }\left\{\begin{array}{l}x\text{ mols.}\\\text{of carbon}\\\text{dioxide ;}\end{array}\right.$$

or,

$$\left.\begin{array}{c}\text{1 mol. of carbon}\\\text{monoxide}\end{array}\right\}\text{ unites with }\left\{\begin{array}{c}\text{HALF A MOL.}\\\text{of oxygen}\end{array}\right\}\begin{array}{c}\text{to}\\\text{give}\end{array}\left\{\begin{array}{l}\text{1 mol.}\\\text{of carbon}\\\text{dioxide.}\end{array}\right.$$

In other words, the oxygen molecule appears to split up into two halves, each half combining with a molecule of carbon monoxide to form a molecule of the dioxide. If, however, the oxygen molecule consists of a single atom of oxygen, we cannot allow that such a thing is possible, without throwing over the central idea of the atomic theory.

Other Examples.—There are many other cases

which might be quoted in which one volume of a gas divides itself into two volumes of gaseous product; *e.g.*:

Nitric Oxide ("Nitric Gas").—We find experimentally that

1 vol. of nitrogen + 1 vol. of oxygen give 2 vols. of nitric oxide.

(Actually, this is found indirectly, as shown in the previous chapter.) If, then, equal volumes of all three gases contain equal numbers of molecules, 1 volume of any of them containing, say, x molecules, we obtain

x mols. of nitrogen + x mols. of oxygen give 2x mols. of nitric oxide; or

1 *mol. of nitrogen +* 1 *mol. of oxygen give* 2 *mols. of nitric oxide.*

Here both the molecule of nitrogen and the molecule of oxygen appear to split into two parts.

Formation of Steam.—To drive the point completely home, we may put the same argument in a slightly different form. When hydrogen and oxygen combine, a molecule of the product, steam, cannot possibly contain *less* than one atom of oxygen. If, therefore, the molecule of oxygen consists of a single atom of oxygen (which is regarded as incapable of splitting up),

1 *mol. of oxygen might give* 1 *mol. of steam;* it could not possibly give more.

Whence

x mols. of oxygen might give x mols. of steam; they could not possibly give more.

So that

1 *volume of oxygen might give* 1 *volume of steam;* it could not possibly give more.

But actually we find that

1 volume of oxygen gives 2 volumes of steam;

so that we reach the same result as before, namely, that the oxygen molecule appears to split into two parts, which is impossible if it consists of a single atom.

Other examples quoted by Avogadro are

3 volumes of hydrogen + 1 vol. of nitrogen = 2 vols. of ammonia ;

2 vols. of nitrogen + 1 vol. of oxygen = 2 vols. of nitrous oxide.

On reflection, it will be seen that the first of these involves the assumption that the molecules *both of nitrogen and of hydrogen* split into two parts ; the second, that the molecule of oxygen splits into two parts. (In no case quoted does the elementary molecule appear to divide itself into *more* than two parts.)

Avogadro's Solution of the Difficulty.—The preceding considerations have shown us that in order to apply the atomic theory of matter to Gay-Lussac's law, it appears to be necessary to suppose that the individual particles of the elementary gases, hydrogen, oxygen, and nitrogen, are capable of splitting up into at least two parts. We have also seen that Dalton had clearly perceived this before Gay-Lussac published his memoir ; and that he had been led in consequence to reject Gay-Lussac's law altogether. It must be remembered that in those days it was very difficult to conduct gas analyses with accuracy ; and, in Dalton's opinion, the " simple ratios " were obtained by reducing the actual experimental figures to round numbers in an unjustifiable manner. As he started with a strong prejudice, on logical grounds, against Gay-Lussac's law, the experimental figures did not in themselves demonstrate the truth of the law sufficiently strongly to convince him against his will.

Avogadro, however, showed that it was possible to reconcile the idea of a chemically indivisible atom with Gay-Lussac's law, *by supposing that the individual particles*

of elementary gases did not consist of single atoms of the elements, but of two or more atoms of the element combined together so as to form a single particle. When chemical combination occurred, these small clusters of atoms broke up into two or more parts ; the maximum number of parts into which a given cluster could break was of course equal to the number of atoms in the cluster.

If, armed with this new conception, we examine the examples given above in order, we obtain the following :

Oxides of Carbon.—*Experimental Facts :*

$$\left.\begin{matrix}\text{2 vols. of carbon}\\ \text{monoxide}\end{matrix}\right\} + \left\{\begin{matrix}\text{1 vol. of}\\ \text{oxygen}\end{matrix}\right\} = \left\{\begin{matrix}\text{2 vols. of carbon}\\ \text{dioxide}\end{matrix}\right.$$

(NOTE : as before, the modern names, which imply a knowledge of formulæ, have been given to these oxides ; but the reader must not imagine that their formulæ were then known with certainty. The only evidence available at that time was the evidence we have already considered, and are now considering.)

Theoretical Interpretation :

2 molecules of carbon monoxide + 1 molecule of oxygen = 2 molecules of carbon dioxide. The molecule of oxygen splits into two parts ; each molecule of carbon dioxide contains half a molecule of oxygen more than does a molecule of carbon monoxide.

The molecule of oxygen must, therefore, contain *at least* two atoms of oxygen. It might, however, contain 4 atoms, or 6, or 8, etc. ; all we can tell from this one example is that the oxygen molecule can be split up into two parts. The molecule must contain *an even number* of atoms, which is easily seen from the following reasoning :

Suppose the oxygen molecule consisted of three atoms of oxygen. Then, when it divides itself between two molecules of carbon monoxide to form two molecules of the dioxide, one molecule of dioxide will contain *one* atom of oxygen more, and the other *two* atoms more,

than the molecules of monoxide. Hence we should get two kinds of carbon dioxide produced, which is contrary to observation. Hence the oxygen molecule contains an even number of atoms.

Nitric Oxide.—*Experimental Facts :*

1 vol. of nitrogen + 1 vol. of oxygen = 2 vols. of nitric oxide.

Interpretation :

1 mol. of nitrogen + 1 mol. of oxygen = 2 mols. of nitric oxide. The molecules of nitrogen and of oxygen split up into two parts ; each molecule of nitric oxide contains half a molecule of nitrogen and half a molecule of oxygen.

Formation of Steam.—*Experimental Facts :*

2 vols. of hydrogen + 1 vol. of oxygen = 2 vols. of steam.

Interpretation :

2 mols. of hydrogen + 1 mol. of oxygen = 2 mols. of steam. The molecule of hydrogen remains intact, while the molecule of oxygen splits up into two parts ; each molecule of steam contains one entire molecule of hydrogen, and half a molecule of oxygen.

Formation of Ammonia.—*Experimental Facts :*

3 vols. of hydrogen + 1 vol. of nitrogen = 2 vols. of ammonia.

Interpretation :

3 mols. of hydrogen + 1 mol. of nitrogen = 2 mols. of ammonia. 1 molecule of ammonia contains $1\frac{1}{2}$ molecules of hydrogen, and half a molecule of nitrogen.

Formation of Nitrous Oxide.—*Experimental Facts :*

2 vols. of nitrogen + 1 vol. of oxygen = 2 vols. of nitrous oxide.

Interpretation :

2 mols. of nitrogen + 1 mol. of oxygen = 2 mols. of nitrous oxide. 1 molecule of nitrous oxide contains 1 molecule of nitrogen, and half a molecule of oxygen.

Summary of Avogadro's Hypothesis.—It is to be hoped that the reader by now thoroughly grasps the point of Avogadro's theory. The argument has been stated at some length, because of its consummate importance. We might summarise it as follows :

Atoms and molecules combine in simple proportions by numbers; gases combine in simple proportions by volume.

Hence there must be some simple relationship between the volumes of different gases, and the number of atoms or molecules which they contain.

The simplest assumption to make is that equal volumes of all gases, at the same temperature and pressure, contain equal numbers of molecules.

Since many reactions are known in which one volume of an elementary gas splits up into two or more volumes of a gaseous product, we must suppose that the individual particle of such a gas is capable of splitting up into two or more parts. This may be reconciled with the indivisibility of the atom by supposing that the individual particle of an elementary gas may consist of two or more atoms united together, the atoms becoming separated when the gas undergoes a reaction of this type. A particle consisting of two atoms could split into two parts; one of three, into three; and so on.

In all the cases we have considered (which are those given by Avogadro in his paper) we never find one volume of a gas giving *more* than two volumes of gaseous product. Avogadro was careful to point out that this in itself does not *prove* that the molecules of these gases contain only two atoms:

"In all these cases there is a division of the molecule into two; but it is possible that in other cases the division might be into 4, 8, etc."

A clear distinction must therefore be drawn between the atom and the molecule. It was a failure to do so which later resulted in much confusion. The following definitions must be adopted:

ATOM: *The smallest particle of an element which can*

take part in a chemical change. It cannot be split up into smaller particles by chemical means.

MOLECULE: *The smallest particle of an element or compound which naturally exists in the free state.*

In the case of elements, the molecule may consist of two or more atoms of the element held together by an attractive force; these atoms remain held together unless separated as the result of a chemical action between the element and some other substance.

Having established these definitions, we may state Avogadro's hypothesis as follows:

EQUAL VOLUMES OF ALL GASES, AT THE SAME TEMPERATURE AND PRESSURE, CONTAIN EQUAL NUMBERS OF MOLECULES.

Dalton's Theory and Avogadro's Hypothesis.—There has been a considerable amount of discussion in the past as to which of these two is really more fundamental. This discussion, though historically interesting, is rather too academic for us; the reader who wishes to pursue the matter further will find an able account in the monograph *Avogadro and Dalton: The Standing in Chemistry of their Hypotheses*, by A. N. Meldrum.* To the present writer it appears that the whole matter may be fairly summarised in the following words:

Dalton's theory, *as he first conceived it*, was too narrow; and he was unable to reconcile it with Gay-Lussac's law, since he held, with what seems to us now very like sheer obstinacy, that the ultimate particles of elementary gases could not be divided. Avogadro's conception of the molecule resolved this difficulty; he retained the idea of the indivisible atom, an idea which he probably owed in the first place to Dalton, since he mentions Dalton's theory several times in the course of his paper; but by supposing that the individual particles of elementary gases

* Aberdeen University Press (out of print).

may contain two or more such atoms, he rendered it theoretically possible for such a particle to split up into two or more parts.

The strong points of Dalton's theory were that it provided a satisfactory explanation of the laws of constant, multiple, and reciprocal proportions ; the usefulness of Avogadro's hypothesis we shall shortly examine. Dalton's views had to be modified ; but it is at least doubtful if, but for his establishment of the atomic theory on a firm *experimental* basis, Avogadro's hypothesis would have arisen when it did.

APPENDIX TO CHAPTER X

A Deduction from Avogadro's Hypothesis.—Avogadro pointed out a consequence of his hypothesis which afterwards became of great importance in the hands of Cannizzaro. Consider equal volumes of two gases at the same temperature and pressure. Both volumes will contain equal numbers of molecules (say n molecules). If the weights of these volumes of gases be now compared, the following result is obtained :

$$\frac{\text{Weight of a given volume of a gas A}}{\text{Weight of the same volume of a gas B}}$$

$$\text{(both being at the same temperature and pressure)}$$

$$= \frac{\text{Weight of } n \text{ molecules of A}}{\text{Weight of } n \text{ molecules of B}}$$

$$= \frac{\text{Weight of ONE molecule of A}}{\text{Weight of ONE molecule of B}}.$$

The relative weights of these two equal volumes of gases hence gives us the relative weights of the molecules of which the gases are composed.

The uses which can be made of this deduction are dealt with in the next chapter.

References

Alembic Club Reprints, No. 4: *Foundations of the Molecular Theory.* Comprising papers and extracts by John Dalton, Joseph Louis Gay-Lussac, and Amadeo Avogadro. 1808–1811.

Extracts from these and other papers will also be found in the book *Cambridge Readings in the Literature of Science*, by W. C. Dampier-Whetham. (Camb. Univ. Press.)

Exercises on Chapter X

1. Write a short account (about 400 words) of the evidence and reasoning which led to Avogadro's hypothesis.

2. What do you consider to be the essential features of (*a*) Dalton's theory, (*b*) Avogadro's hypothesis, and why should they be considered as marking important advances in scientific knowledge?

3. Summarise briefly the subject-matter of Chaps. V (B), VI, VII, VIII, IX, and X, distinguishing clearly between those portions of it which deal with established laws, and those which are concerned with theories or hypotheses

4. The following table gives the relationship between a given volume of hydrogen and the corresponding volumes of gaseous products of hydrogen, the latter being found by direct synthesis, or by other methods less direct:

Compound.	Vol. of Hydrogen.	Corresponding Vol. of Gaseous Product (at same Press. and Temp.).
Steam	.. 1	1
Hydrogen chloride ..	.. 1	2
Hydrogen bromide ..	.. 1	2
Ammonia	.. 3	2
Phosphine	.. 3	2

From these data, what provisional conclusion may be reached regarding the probable composition of the hydrogen molecule? Give fully the reasons for your answer.

5. (*a*) Carbon burns in oxygen, forming a gaseous oxide which occupies the same volume as the original oxygen.

(*b*) When hydrogen sulphide is decomposed by electric sparks, solid sulphur is deposited, and the hydrogen produced occupies the same volume as the original hydrogen sulphide.

(*c*) When phosphine is treated as in (*b*), phosphorus is deposited, 2 volumes of phosphine yielding 3 volumes of hydrogen.

Making no assumptions beyond Avogadro's hypothesis, state clearly how much information the above facts convey regarding the molecular composition of the respective compounds.

CHAPTER XI

THE WORK OF CANNIZZARO

IN 1858 there appeared, in the Italian scientific journal *Il Nuovo Cimento*, a long letter from Professor Stanislao Cannizzaro, entitled " Sunto di un Corso di Filosofia Chimica, fatto nella Università di Genova " (Summary of a Course of Theoretical Chemistry, held in the University of Genoa), which proved to be one of the most important papers ever produced in the history of chemistry. We shall deal with the effects of this paper on contemporary chemistry in the next chapter ; we are concerned here with Cannizzaro's actual argument.

" I consider," he began, " that the progress of science which has taken place in recent years has confirmed the hypotheses of Avogadro, of Ampère and of Dumas regarding the similar constitution of substances in the gaseous state, that is, that equal volumes of them, whether they are elementary or compound, contain equal numbers of molecules ; not, however, equal numbers of atoms, as the molecules of different substances, or those of the same substance in different states, may contain different numbers of atoms, whether these are of the same kind, or of different kinds."

Cannizzaro then proceeded to outline the various lectures which he gave in his course of chemistry ; the first four lectures dealt with the history of theoretical chemistry, including, in the second lecture, a reference to the refusal of Dalton to accept Avogadro's hypothesis, since Dalton was unable to admit that

" when two substances form a single compound, one molecule of one and one molecule of the other, instead of uniting

together in a single molecule, may change into two (molecules) of the same kind."

He went on :

" I begin in the fifth lecture to apply the hypothesis of Avogadro and of Ampère to determine the weights of molecules, *even before their composition is known.*"

There follows a reference to the conclusion that the densities of gases must be proportional to the weights of their molecules (*cf.* p. 108). For the purpose of determining relative molecular weights, it is better to choose as a standard unit the density of a pure elementary gas rather than that of a mixture of gases such as air. Hydrogen, being the lightest gas, naturally suggests itself as the standard substance ; and the densities of other gases are thus referred to that of hydrogen. This gives us the " Vapour Density," defined as follows :

$$\text{Vapour Density} = \frac{\text{Weight of a given vol. of gas}}{\text{Weight of the same vol. of hydrogen}}$$

both gases being measured at the same temperature and pressure.

(Since all gases expand and contract equally with respect to temperature and pressure, it does not matter what these are, provided they are the same in both cases.)

It follows, from the argument given on p. 108, that the Vapour Density of a gas must be equal to the ratio

$$\frac{\text{Weight of a single molecule of the gas}}{\text{Weight of a single molecule of hydrogen}}.$$

This conclusion, of course, is directly dependent upon Avogadro's hypothesis.

Cannizzaro then gives the table which follows, in which figures are arranged in two columns. The first column gives the vapour density, or (which comes to the same

thing) the weights of the molecules of the various elements and compounds, compared with that of a molecule of hydrogen. The second column gives a similar ratio, except that densities are referred to hydrogen=2 instead of 1. That is, the figures in the second column are all double the corresponding figures in the first column; and they will be equal to the ratio

$$\frac{\text{Weight of a molecule of gas or vapour}}{\text{Weight of HALF A MOLECULE of hydrogen}}.$$

This quantity we shall call the MOLECULAR WEIGHT *of the gas or vapour.* The reason for splitting up the molecule of hydrogen into two half-molecules will become clear shortly.

Name of substance.	Vapour Density. (*i.e.* weights of the molecules referred to the weights of a whole molecule of Hydrogen taken as unity).	Molecular Weight. [=Vapour Density × 2]. (*i.e.* weights of the molecules referred to the weight of half a molecule of Hydrogen taken as unity).
Hydrogen	1	2
Ordinary oxygen ..	16	32
Electrified oxygen ..	64	128
Sulphur below 1000°	96	192
Sulphur above 1000°	32	64
Chlorine	35·5	71
Bromine	80	160
Arsenic	150	300
Mercury	100	200
Water	9	18
Hydrogen chloride ..	18·25	36·5
Acetic acid	30	60

(" Electrified oxygen," of course, means ozone; but the value for the density is incorrect.)

To make this perfectly clear, we will repeat that the *first* column of figures represents the *experimentally determined* ratio

$$\frac{\text{Weight of a given vol. of gas or vapour}}{\text{Weight of the same vol. of hydrogen}},$$

both at the same temperature and pressure; hence, by Avogadro's hypothesis, this equals the ratio

$$\frac{\text{Weight of a single molecule of gas or vapour}}{\text{Weight of a single molecule of hydrogen}};$$

the *second* column of figures, which is obtained by doubling the first, gives the ratio

$$\frac{\text{Weight of a single molecule of gas or vapour}}{\text{Weight of HALF a molecule of hydrogen}}.$$

For example, a molecule of chlorine gas weighs 35·5 times as much as a molecule of hydrogen, or 71 times as much as half a molecule of hydrogen.

These figures, as Cannizzaro points out, can be reached simply by determining the relative densities of the gases; no chemical analysis is necessary, and one need not even know if the various substances are elements or compounds.

The next step is to examine the composition of the molecules. We have two types to deal with:

(*a*) Molecules made up entirely of a single element (*e.g.* the first nine in the above table).

(*b*) Molecules of compounds. In the case of a compound molecule, we can find, by analysis, the percentage composition by weight of the given compound. From the vapour density of the compound, we can find its molecular weight (twice the vapour density). *We can then proceed to split up this molecular weight into separate parts representing the weights of the different elements present in a molecular weight of the compound.*

A couple of examples will make it clear how this is done.

Water.—The percentage composition by weight of water is

11·1 per cent. hydrogen;
88·9 per cent. oxygen.

We have seen that the molecular weight of water is 18. Hence, in 18 parts by weight of water there will be

$$18 \times \frac{11 \cdot 1}{100} = 2 \text{ parts by weight of hydrogen, and}$$

$$18 \times \frac{88 \cdot 9}{100} = 16 \text{ parts by weight of oxygen.}$$

Acetic Acid.—This has the following percentage composition:

40·0 per cent. carbon;
6·7 per cent. hydrogen;
53·3 per cent. oxygen.

The molecular weight is 60. Hence, in 60 parts by weight of acetic acid there will be

$$60 \times \frac{40}{100} = 24 \text{ parts by weight of carbon;}$$

by similar calculation we find that there will be

4 parts by weight of hydrogen, and
32 parts by weight of oxygen.

A charming passage in Cannizzaro's paper explains how he " rubs in " the meaning of these figures into the minds of his pupils. It is to this effect:

Let us imagine that we could show that the half-molecule of hydrogen actually weighs a millionth of a milligram. Then the " molecular weight " becomes the weight of a single molecule, measured in millionths of a milligram. Thus, in the above two examples, a molecule of water will weigh 18 millionths of a milligram; and this weight will be made up of 2 millionths of a milligram of hydrogen, and 16 millionths of a milligram of oxygen. Again, the molecule of acetic acid, weighing in all 60 millionths of a milligram, will be made up of 24 millionths of a milligram of carbon, 4 of hydrogen, and 32 of oxygen.

In this way Cannizzaro led his pupils on " to form a clear idea of the comparability of these numbers, whatever may be the actual value of the common unit " (that

is to say, whatever may be the actual weight of half a molecule of hydrogen). "Once this device has served its purpose, I hasten to destroy it by pointing out that one cannot in fact know the actual value of this unit; but the clear conceptions remain in the minds of the pupils, whatever may be their degree of instruction in mathematics. I act rather like the engineers, who destroy the wooden scaffolding which has served to construct a bridge as soon as the latter can stand by itself."

He then adds:

"But I fear you will say to me: 'Is it worth the trouble, and the waste of time and ink, to tell me about such a vulgar expedient?' I must confess that I paused to do so, because I am attached to this pedagogic device, having had such success with it amongst my pupils; therefore I make so bold as to recommend it to all those who, like myself, have to teach chemistry to young people not much versed in the comparison of quantities."

Cannizzaro's table is reproduced herewith.*

Deductions from the Table.—On studying this table, a most striking and important fact at once emerges.

If we compare the various weights of a given element which are contained in a molecular weight, either of the free element or of its different compounds, we find that they are all multiples by a whole number (including unity) of some constant quantity, which has a characteristic value for the particular element.

There seems, then, for every element, to be a certain characteristic weight, representing the smallest weight of the element which ever enters into a molecular weight of any of its compounds. Since the atom is the smallest particle of an element which can enter into combination, this minimum weight may, therefore, be regarded as the atomic weight of the element.

* Reproduced by kind permission of the Alembic Club.

Name of Substance.	Weight of one volume, *i.e.*, weight of the molecule referred to the weight of half a molecule of Hydrogen = 1.	Component weights of one volume, *i.e.* component weights of the molecule, all referred to the weight of half a molecule of Hydrogen = 1.	
Hydrogen	2	2 Hydrogen	
Oxygen, ordinary ..	32	32 Oxygen	
,, electrised ..	128	128 ,,	
Sulphur below 1000°	192	192 Sulphur	
,, above 1000° (?)	64	64 ,,	
Phosphorus	124	124 Phosphorus	
Chlorine	71	71 Chlorine	
Bromine	160	160 Bromine	
Iodine	254	254 Iodine	
Nitrogen	28	28 Nitrogen	
Arsenic	300	300 Arsenic	
Mercury	200	200 Mercury	
Hydrochloric Acid ..	36·5	35·5 Chlorine	1 Hydrogen
Hydrobromic Acid ..	81	80 Bromine	1 ,,
Hydriodic Acid ..	128	127 Iodine	1 ,,
Water	18	16 Oxygen	2 ,,
Ammonia	17	14 Nitrogen	3
Arseniuretted Hyd...	78	75 Arsenic	3 ,,
Phosphuretted Hyd.	35	32 Phosphorus	3 ,,
Calomel	235·5	35·5 Chlorine	200 Mercury
Corrosive Sublimate	271	71 ,,	200 ,,
Arsenic Trichloride..	181·5	106·5 ,,	75 Arsenic
Protochloride of Phosphorus	138·5	106·5 ,,	32 Phosphorus
Perchloride of Iron ..	325	213 ,,	112 Iron
Protoxide of Nitrogen	44	16 Oxygen	28 Nitrogen
Binoxide of Nitrogen	30	16 ,,	14 ,,
Carbonic Oxide ..	28	16 ,,	14 Carbon
,, Acid ..	44	32 ,,	12 ,,
Ethylene	28	4 Hydrogen	24 ,,
Propylene	42	6 ,,	36 ,,
Acetic Acid, hydrated	60	4 ,, 32 Oxygen 24 Carbon	
,, anhydrous..	102	6 Hydrogen 48 Oxygen 48 Carbon	
Alcohol	46	6 Hydrogen 16 Oxygen 24 Carbon	
Ether	74	10 Hydrogen 16 Oxygen 48 Carbon	

Since, according to Cannizzaro's scheme, the unit of weight is taken as the weight of half a molecule of hydrogen the *atomic weight* of an element found by this method is equal to the ratio

$$\frac{\text{Weight of an atom of the element}}{\text{Weight of half a molecule of hydrogen}}.$$

In considering some particular cases in detail, we will take first the compounds formed by hydrogen, as these are of especial importance.

Compounds of Hydrogen.—From the preceding table, the following figures may be taken :

Substance.	Weight of Hydrogen in a molecular weight. (Unit of weight = half the weight of a Hydrogen molecule.)	
Free hydrogen	2	= 2 × 1
Hydrogen chloride	1	= 1 × 1
Hydrogen bromide	1	= 1 × 1
Hydrogen iodide	1	= 1 × 1
Hydrogen cyanide	1	= 1 × 1
Water	2	= 2 × 1
Hydrogen sulphide	2	= 2 × 1
Formic acid	2	= 2 × 1
Ammonia	3	= 3 × 1
Hydrogen phosphide.. ..	3	= 3 × 1
Acetic acid	4	= 4 × 1
Ethylene	4	= 4 × 1
Ether	10	= 10 × 1

The significance of this will be clear on a moment's reflection. The weights of hydrogen in molecular weights of these substances are always multiples by a whole number of the weight of half a molecule of hydrogen. Hence, it appears that THE SMALLEST QUANTITY OF HYDROGEN WHICH EVER ENTERS INTO COMBINATION IS HALF A MOLECULE OF HYDROGEN ; FROM WHICH IT FOLLOWS THAT HALF A MOLECULE OF HYDROGEN IS IDENTICAL WITH THE ATOM OF HYDROGEN.

Instead, therefore, of "the weight of half a molecule of hydrogen," we can write "the weight of an atom of hydrogen," obtaining the following definitions:

Molecular Weight (= 2 × Vapour Density)

$$= \frac{\text{Weight of a molecule of element or compound}}{\text{Weight of an ATOM of hydrogen}},$$

and

$$\text{Atomic Weight} = \frac{\text{Weight of an atom of element}}{\text{Weight of an atom of hydrogen}}.$$

In view of its importance, it is desirable to have some corroborative evidence that the molecule of hydrogen contains two atoms (*i.e.* that the half-molecule of hydrogen is identical with the atom of hydrogen). This will be found on p. 123.

Oxygen Compounds.—The table gives us the following data:

Substance.	Weight of Oxygen in a molecular weight.	
Free oxygen ..	32	= 2 × 16
Water	16	= 1 × 16
Ether	16	= 1 × 16
Acetic acid	32	= 2 × 16
etc., etc.		

Whence it appears (*a*) that the atomic weight of oxygen is 16 (since the smallest weight of oxygen entering into combination is 16 times the weight of an atom of hydrogen), and (*b*) that the molecule of free oxygen contains two atoms.

Chlorine Compounds.—

Substance.	Weight of Chlorine in a molecular weight.	
Free chlorine ..	71	= 2 × 35·5
Hydrogen chloride ..	35·5	= 1 × 35·5
Corrosive sublimate..	71	= 2 × 35·5
Arsenic chloride ..	106·5	= 3 × 35·5
Tin chloride.. ..	142	= 4 × 35·5
etc., etc.		

The atomic weight of chlorine is thus seen to be 35·5, and chlorine gas is diatomic.

To sum up, we may say that Cannizzaro's method gives us a means of determining the weights of elements present in molecular weights of their volatile compounds. It will be found that the weights of a given element present in molecular weights of its various compounds are always multiples by a whole number of a constant weight, w. Since w, therefore, represents the smallest weight of the element ever entering into a molecular weight of any of its compounds, it may be regarded as the atomic weight of the element. This should not be regarded as a separate *definition* of atomic weight, but as a consequence of the atomic theory and of Avogadro's hypothesis, applied to our previous definitions of vapour density, molecular weight, and atomic weight.

It is evident that the compounds considered must be capable of being vaporised without decomposition; the means whereby atomic weights of elements forming no such compounds can be found will be dealt with in the chapters which follow. Evidently, in order to be reasonably sure that we have really found the smallest weight of the element ever entering into combination, we must take as many compounds of that element as possible; if, for example, the only compounds of chlorine we had examined had been corrosive sublimate and tin chloride, we might come to the erroneous conclusion that the atomic weight of chlorine was 71. The larger the number of compounds examined, the surer we can be that the smallest quantity of the element which we find to enter into combination is really the atomic weight.

One point may be mentioned. A determination of the weight of an element present in a molecular weight of *one* of its compounds will give us at once the *maximum* possible value of the atomic weight. For since the atom is the smallest quantity of an element which can

exist in a molecule of any of its compounds, so the smallest weight of an element found to enter into combination cannot be less than an atomic weight of the element.

An example will make this clear. Take the four oxygen compounds given above. The weights of oxygen in their molecular weights (which include that of free oxygen) are all multiples of 16. Therefore the atomic weight of oxygen cannot be *greater* than 16, though it might be less. If the atomic weight is 16, the four substances contain 2, 1, 1, and 2 atoms of oxygen respectively in their molecules. Now, it is conceivable that a compound might be found which only contained eight parts of oxygen in a molecular weight. In that case, the atomic weight of oxygen could not be greater than 8, and the other four substances would contain respectively 4, 2, 2, and 4 atoms of oxygen in the molecule. The large number of oxygen compounds examined by now, renders such a possibility very unlikely. If water were the only known volatile compound of oxygen, however, the determination if its vapour density and percentage composition would enable us to decide that the atomic weight of oxygen could not be *greater* than 16.

A case in which a single determination of this kind has been instrumental in deciding the atomic weight of an element is that of beryllium, to which reference will be found later on.

Atomic Weights by Cannizzaro's Method.—Most of the principal results have been given in the table on p. 117. As a result of vapour density measurements alone, Cannizzaro was able to calculate by his method atomic weights which agree to the nearest whole number with those at present adopted for the following elements :

H, O, N, Cl, Br, I S, P,* As (the last three from their hydrides) ;

and to give a provisional value of 200 for mercury—this will be considered later on p. 145.

Using these values, the molecular state of gaseous elements may be deduced as follows :

	Molecular Weight.	Atomic Weight.	Number of atoms in the molecule.
Hydrogen	2	1	2
Oxygen	32	16	2
Nitrogen	28	14	2
Chlorine	71	35·5	2
Bromine	160	80	2
Iodine	254	127	2
" Sulphur below 1000° "	192	32	6
" Sulphur above 1000° "	64	32	2
*Phosphorus	124	32	4
Arsenic	300	75	4
Mercury	200	200	1

The Atomic Weight of Carbon.—This provides an interesting application of Cannizzaro's method. He says :

" . . . Above all, I endeavour to implant firmly . . . the difference between molecule and atom. One can, in fact, know the atomic weight of an element without knowing the weight of its molecule ; this is the case with carbon. A great number of the compounds of this substance being volatile, one can compare their molecular weights and their compositions, and it is found that the quantities of carbon contained in them are all whole multiples of 12, which quantity is therefore the atom expressed by the symbol C ; but not being able to determine the vapour density of free carbon, we have no means of knowing the weight of its molecule, and therefore cannot know how many atoms are contained in it."

Analysis of some typical carbon compounds yields the following results :

* The value for phosphorus is not quite accurate ; the atomic weight now adopted is 30·8 (H = 1).

Name of the Carbon compound.	Weights of their molecules compared with that of the Hydrogen atom.	Weights of the components of the molecule using same unit.	Formulæ taking H=1, C=12, O=16, S=32.
Carbonic oxide ..	28	12 C, 16 O	CO
Carbonic acid ..	44	12 C, 32 O	CO_2
Sulphide of carbon ..	76	12 C, 64 S	CS_2
Marsh gas	16	12 C, 4 H	CH_4
Ethylene	28	24 C, 4 H	C_2H_4
Propylene	42	36 C, 6 H	C_3H_6
Ether	74	48 C, 10 H, 16 O	$C_4H_{10}O$
etc., etc.			

Thus, though carbon itself is non-volatile, we can determine its atomic weight, since it forms many volatile compounds, the quantities of carbon contained in molecular weights of these compounds being always multiples of 12.

Evidence that the Hydrogen Molecule contains Two Atoms.—(1) When the molecular weights and percentage compositions of volatile hydrogen compounds are determined, it is found that the smallest quantity of hydrogen entering into combination as a complete unit is half a molecule of hydrogen. This indicates that the half-molecule of hydrogen is the smallest quantity of hydrogen capable of existence; *i.e.* that it is identical with the atom of hydrogen. (See above, p. 118.)

(2) When hydrogen combines with chlorine to form hydrogen chloride, 1 volume of hydrogen gives 2 volumes of hydrogen chloride. Hence, by Avogadro's hypothesis, 1 molecule of hydrogen chloride contains half a molecule of hydrogen.

Hydrogen chloride dissolves in water, forming hydrochloric acid. This acid is monobasic; *i.e.* the hydrogen in it can only be replaced by metals in one stage. Hence, probably, the molecule of hydrogen chloride contains only one atom of hydrogen, which is thus identical with the half-molecule of hydrogen.

(3) Making certain assumptions, it is possible to calculate that the ratio of the specific heats of a diatomic gas, measured at constant pressure and constant volume respectively, should be equal to 1·4. This value is actually found for hydrogen. The reasoning involved is highly theoretical, and its validity has been questioned. Nevertheless, the agreement with the theoretical value may be taken as corroborative evidence that the hydrogen molecule contains two atoms. (For discussion of this, see Chap. XV.)

(4) No observations as yet made are incompatible with the view that hydrogen gas is diatomic.

It will be seen that the "proof" of the diatomicity of hydrogen rests largely upon negative evidence. Thus, in (1) the fact that no compound has been yet found the molecule of which contains less than half a molecule of hydrogen does not preclude the possibility of a compound being discovered containing less hydrogen in its molecule. Again, argument (2) rests on the fact that no acid chloride has as yet been prepared. The degree of certainty which we can place upon (3) is fully considered later on; but the certainty cannot be called absolute. Argument (4) is, of course, frankly based on negative evidence.

Nevertheless, there is a vast amount of this evidence. Thousands of hydrogen compounds (including those of which the molecular weights can be found by methods given in later chapters) have been examined by method (1); hundreds of different chlorides are known, and in no case is there any reason to suspect the correctness of our views. When "circumstantial evidence" (that is, indirect evidence not based on rigid proof) has accumulated a sufficient number of instances all of which point to the same conclusion, it becomes strong enough to convince the most hard-headed jury. Though we must in honesty admit the possibility of the conclusion being wrong, the possibility in this case is so faint as to be almost inconceivable. Meanwhile, we must consider that we

are justified in assuming the conclusion to be true, until unmistakable evidence can be produced to the contrary.

NOTE.—It may be added that the principal evidence for the diatomicity of oxygen, chlorine, nitrogen, etc., is similar to that given in paragraph (1) above (see Table on p. 122).

SUMMARY OF CHAPTER XI

It is hardly necessary to emphasise the enormous importance of Cannizzaro's work. For the first time a method had been demonstrated, based on sound theoretical reasoning, for finding the atomic weights of those elements which formed compounds which were either gaseous at ordinary temperatures, or which can be vaporised without decomposition. It may be useful to summarise here the essential steps involved.

(1) The term "Vapour Density" is first defined as follows:

$$\text{Vapour Density} = \frac{\text{Weight of a given volume of gas or vapour}}{\text{Weight of the same volume of hydrogen}},$$

both being measured at the same temperature and pressure.

Since, by Avogadro's hypothesis, these equal volumes of gases contain equal numbers of molecules, the vapour density is equal to the ratio

$$\frac{\text{Weight of a single molecule of gas or vapour}}{\text{Weight of a single molecule of hydrogen}}.$$

(2) In order to express relative weights of molecules by means of numbers, it is necessary to take a standard unit of weight to which the other weights are referred. This unit of weight is taken as the weight of half a molecule of hydrogen, and molecular weight is *defined* as follows:

Molecular Weight

$$= \frac{\text{Weight of a molecule of element or compound}}{\text{Weight of half a molecule of hydrogen}};$$

and it follows from the previous reasoning that

$$\text{Molecular Weight} = 2 \times \text{Vapour Density}.$$

Hence, experimental determinations of vapour density provide the necessary data for calculating the molecular weights of volatile elements and compounds.

(3) By this means we proceed to find the molecular weights of as many as possible of the compounds which are formed by a given element. By ascertaining also the percentage compositions of these compounds, we may calculate the weights of the element present in their molecular weights.

It is found that if this is done, the weights of an element present in molecular weights of its compounds are always multiples by a whole number (including unity) of a fixed quantity, characteristic of the element. Since, therefore, this fixed quantity represents the smallest weight of the element ever entering into a molecular weight of any of its compounds, it may be called the atomic weight of the element, where atomic weight is defined by the ratio

$$\frac{\text{Weight of an atom of the element}}{\text{Weight of half a molecule of hydrogen}}.$$

(4) Examining hydrogen compounds in this way, it is found that the smallest quantity of hydrogen ever entering into combination is half a molecule of hydrogen. Hence half a molecule of hydrogen is identical with an atom of hydrogen, and the above definitions of molecular and atomic weights become

Molecular Weight

$$= \frac{\text{Weight of a molecule of element compound}}{\text{Weight of an atom of hydrogen}}.$$

$$\text{Atomic Weight} = \frac{\text{Weight of an atom of the element}}{\text{Weight of an atom of hydrogen}}.$$

(5) Cannizzaro was able in this way to assign probable values to the atomic weights of the following elements:

Element.	Atomic Weight (=weight of the atom, compared with the weight of a Hydrogen atom).	
Hydrogen	1	
Oxygen	16	
Nitrogen	14	
Chlorine	35·5	
Bromine	80	
Iodine	127	
Phosphorus	32	(Modern value 31, to nearest whole number.)
Arsenic	75	
Sulphur	32	
Carbon	12	
Mercury	200	(See also Chap. XII (B).)

References

Alembic Club Reprints, No. 18: *Sketch of a Course of Chemical Philosophy*, by Stanislao Cannizzaro. 1858.

Exercises on Chapter XI

(1) In the following tables will be found the vapour densities of various compounds formed by a given element, together with the respective percentages by weight of the element contained in the compounds. State what conclusions may be drawn from them regarding the probable atomic weight of the element concerned.

(*a*) Compounds of Sulphur.

Compound.	Per cent. S in compound.	Vapour Density of compound.
Hydrogen sulphide	94	17
Carbon disulphide	84·2	38
Ethyl sulphide	35·6	45
Carbon oxysulphide ..	53·3	30
Sulphur dioxide	50	32

(*b*) Compounds of Phosphorus.

Compound.	Per cent. P in compound.	Vapour Density of compound.
Phosphorus vapour ..	.. 100	62
Phosphine	.. 91·2	17
Triethyl phosphine ..	.. 26·3	59
Phosphorus pentafluoride	.. 24·6	63

(*c*) Compounds of Nitrogen.

Compound.	Per cent. N in compound.	Vapour Density of compound.
Nitrogen gas.. ..	.. 100	14
Ammonia	.. 82·3	8·5
Ethyl nitrate ..	.. 15·4	45·5
Ethyl nitrite	.. 18·7	37·5
Ethyl hyponitrite ..	.. 23·7	59
Hydrazoic acid ..	.. 97·7	21·5

(*d*) Compounds of Carbon.

Compound.	Per cent. C in compound.	Vapour Density of compound.
Acetylene	.. 92·3	13
Ethylene	.. 85·7	14
Ethane	.. 80·0	15
Butane	.. 82·8	29
Naphthalene ..	.. 93·8	64
Propylene	.. 85·7	21

(2) Magnesium ethyl contains 29·3 per cent. of magnesium by weight, and has a vapour density of 41.

What conclusion may be drawn from this regarding the atomic weight of magnesium?

(3) The equivalent weight of beryllium is 4·55. The element resembles aluminium in several respects, and was formerly thought to be trivalent. The vapour density of the chloride was, however, found to be 40. What is the significance of this result?

CHAPTER XII (A)

THE POSITION AFTER DALTON (BEFORE THE APPEARANCE OF CANNIZZARO'S PAPER)

"Confusion worse confounded."
MILTON, *Paradise Lost.*

THE history of the years immediately following the publication of Dalton's theory is extremely interesting, and merits a longer study than we are able to give it here. The main problem of chemistry was the determination of the relative weights of atoms, as the first step to the determination of the formulæ of compounds. Dalton's work had convinced nearly every one of the existence of atoms, and of the fact that atoms combined in quite simple ratios. But how could these ratios be found?

It may not be out of place to repeat that the *equivalent weights* of the elements could be determined quite apart from theory; these are simply the proportions by weight in which the elements combine, and can be found by various methods to a degree of accuracy only limited by the experimental skill of the time. The problem which perplexed Dalton's contemporaries and successors lay in finding the whole number by which the equivalent weight must be multiplied in order to give the atomic weight; and any means which led independently to an *approximate* value for the atomic weight were sufficient for this purpose.

During the first half of the nineteenth century, three main systems of chemistry were developed: those of Berzelius, of Gmelin, and of Gerhardt and Laurent. Of these that of Berzelius was the earliest, being put forward in its various forms from about 1815 onwards, while

that of Gmelin followed about 1840, and the third from 1842 onwards. All three were, of course, superseded by the system of Cannizzaro, which became widely known in 1860. The three systems had many points in common; and we cannot spare the time to distinguish them in detail from one another, but must content ourselves with considering a few of their main features.

The refusal of Dalton to admit the truth of Gay-Lussac's law was not shared by all other chemists; thus, in 1812, Berzelius wrote to Dalton as follows:

> "There are parts (of the atomic theory) . . . which demand a little alteration. That part, for example, which obliges you to declare as inaccurate the experiments of Gay-Lussac, on the volumes of gases which combine. I should have thought rather that these experiments were the finest proof of the probability of the atomic theory."

But Berzelius himself was not conspicuously successful in his attempts to apply Gay-Lussac's law to the pressing problem of atomic weight determination. He began by supposing that equal volumes of elementary gases, at the same temperature and pressure, contained equal numbers of atoms; but maintained that this did not hold for the molecules of compound gases. While illogical, this led him to a number of formulæ which were nearer to the truth than Dalton's; the fact, for example, that 2 volumes of hydrogen combine with 1 of oxygen caused him to write the formula of water as H_2O, thereby giving oxygen the atomic weight of 16, whereas Dalton had written HO for water. Later, however, determinations of the density of phosphorus, arsenic, and mercury vapours led to results which contradicted Berzelius' theory in its original form, and led him to the most improbable suppositions, such as the existence of a "chemical atom" which could be divided into two "physical atoms." About this time the system was largely abandoned by other chemists, since

"even the authority of Berzelius was inadequate to recommend a system that had become a welter of conflicting ideas and principles" (Meldrum, *Avogadro and Dalton*).

Some use of Avogadro's hypothesis was made by Gerhardt and Laurent, and many of their atomic weights are in agreement with modern values; but though their system was on the whole an advance on that of Berzelius, particularly in the growing subject of organic chemistry, it still lacked a satisfactory physical basis. Gerhardt and Laurent adopted the formula of H_2O for water, and regarded this compound as providing the "type" for many others, such as the oxides and hydroxides of metals, the alcohols and ethers, acid anhydrides, and so forth. Thus hydrogen sulphide and sodium oxide were of the "water type," their formulæ being accordingly H_2S and Na_2O. These formulæ led to the correct values of 32 and 23 for the atomic weights of sulphur and sodium respectively. On the other hand, the oxides of zinc and mercury (mercuric), which are now known to possess the formulæ ZnO and HgO, were similarly written Zn_2O and Hg_2O, which led to the values of 37·5 and 100 for the respective atomic weights of the two metals.

Gmelin's system differed considerably from the other two. It is sometimes said that it advocated a return to chemical equivalents, and an abandonment as hopeless of any attempt to find relative atomic weights. This does not appear to be the case (see Meldrum, *loc. cit.*, Chap. XI). Nevertheless, many chemists seem to have grown discouraged at this time by the growing complexity of the various systems, and by the difficulty of deciding between the merits of one and another; and in many respects the "atomic weights" of Gmelin do represent merely chemical equivalents.

In short, the whole period was one of great confusion. Some progress was made however; and in particular three methods of atomic weight determination were developed which afterwards became of first-rate import-

ance. At the time they suffered from the lack of a fundamental method which should serve to co-ordinate them and place them on a secure footing; this, as we shall see later, was just what Cannizzaro was able to supply. These three methods were (*a*) Berzelius' method of "chemical analogy," (*b*) Dulong and Petit's law of atomic heats, and (*c*) Mitscherlich's law of isomorphism. We shall deal with them in this order.

Berzelius' Method of Chemical Analogy.—Berzelius, while welcoming the atomic theory of Dalton at the outset, realised at once that Dalton's rules of combination were arbitrary, and endeavoured to find independent evidence of the constitution of molecules. He was one of the greatest chemists alive; and for more than twenty years after the publication of the *New System* was accepted generally as the greatest living authority on atomic weights.

The principle which we are considering may be expressed quite simply: namely, that *substances which are chemically analogous have similar formulæ.* The method is best understood by taking an example, say that in which he was led to correct his earliest values for the atomic weights of many metals. This involved several steps.

(*a*) *The formula of sulphuric anhydride.*

By an ingenious experiment, Berzelius was able to show that when lead sulphide is converted into lead sulphate, by oxidation with nitric acid, the proportions of lead to sulphur are unchanged, the reaction involving merely addition of oxygen.

Lead oxide and lead sulphide were given the simplest possible formulæ, PbO and PbS respectively (Berzelius was wont to adopt Dalton's idea if no contrary evidence as to the correctness of the resulting formula could be obtained).

From his quantitative results he obtained the following:

100 grms. of lead can be converted into 107·7 grms. of oxide, *or* into 115·42 grms. of sulphide. This weight of sulphide on oxidation gave 146·33 grms. of sulphate.

The amount of oxygen added on conversion of sulphide into sulphate = 30·91 grms., which = 7·7 × 4 (*i.e.* four times the amount of oxygen present in the oxide).

From this it is easy to see that if lead oxide is PbO, and if lead sulphide is PbS, lead sulphate must be $PbSO_4$, and sulphuric anhydride SO_3 (the salt being a compound of oxide + anhydride, PbO,SO_3).

(*b*) *The formula of chromic anhydride.*

Chromic anhydride, which combines with bases to give chromates, resembles sulphuric anhydride in combining with bases containing ⅓ as much oxygen as is contained in an equivalent amount of the anhydride.

Hence, by "chemical analogy," these two anhydrides should have similar formulæ; and if that of sulphuric anhydride is SO_3, that of chromic anhydride will be CrO_3.

(*c*) *The formula of chromic oxide.*

Chromium forms a lower, primarily basic, oxide, which gives rise to the chromic salts. The weights of oxygen combining with a fixed weight of chromium, in chromic anhydride and chromic oxide, are as 2 : 1 respectively.

Hence if the formula of chromic anhydride is CrO_3, that of chromic oxide must be Cr_2O_3.

(*d*) *The formula of ferric oxide.*

Ferric salts resemble chromic salts in their general chemical properties. Hence ferric oxide, by chemical analogy, will have the formula Fe_2O_3.

(*e*) *The formulæ of ferrous oxide, and of other basic oxides.*

The proportions of oxygen combining with a fixed weight of iron are as 3 : 2 in ferric and ferrous oxides respectively.

Hence if the formula of ferric oxide is Fe_2O_3, that of ferrous oxide will be FeO.

A number of other metals—zinc, copper, etc.—form basic oxides, giving rise to salts chemically similar to ferrous salts. Hence we may regard all these oxides as of the general formula MO, where M represents an atom of iron, zinc, copper, etc.

By this chain of reasoning, subsequently confirmed by the discovery of the Law of Isomorphism, Berzelius was led to correct a number of formulæ, as is seen from the following table:

Compound.	Previous Formula (1818).	Corrected Formula (1826).
Chromic anhydride ..	CrO_6	CrO_3
Chromic oxide	CrO_3	Cr_2O_3
Ferric oxide	FeO_3	Fe_2O_3
Ferrous oxide	FeO_2	FeO
Zinc oxide	ZnO_2	ZnO
Nickel oxide	NiO_2	NiO
Copper oxide	CuO_2	CuO
		etc.

Further references to Berzelius' early values for atomic weights (which of course are dependent upon the formulæ assigned to these oxides) will be found in the discussion of Dulong and Petit's law, and the law of isomorphism. It will be seen from the above examples that a useful advance had been made. And yet all this work rests upon somewhat doubtful reasoning. The basis of it is really Dalton's idea, that we should assume the simplest possible formula for a given compound when no evidence appears to the contrary; the main feature of Berzelius' work lies in the fact that he endeavoured to obtain confirmatory evidence of the correctness of these formulæ whenever possible, using his great chemical knowledge as a guide. That Berzelius himself was far from satisfied with the evidence may be seen from the following extract, written in 1828:

"To light upon what is true is a matter of luck, the full value of which is only realised when we can prove that what we have found *is* true. Unfortunately, in these matters the certainty of our knowledge is as yet at so low a level that all we can do is to follow along the lines of greatest probability."

Dulong and Petit's Law of Atomic Heats.—In 1819 Dulong and Petit published a paper entitled "Researches on some Important Points in the Theory of Heat." They had found that, using the atomic weight values given by Berzelius (these were, of course, the earlier values), they obtained the following result:

If the atomic weights and specific heats of elements be multiplied together, values are obtained which are either equal to, or simple multiples of, one another.

It is convenient to coin the term "atomic heat" for the product of specific heat and atomic weight; it represents, numerically, the number of calories necessary to raise one atomic weight, in grams, of the element, through one degree Centigrade.

Dulong and Petit were therefore faced with two alternatives:

(*a*) If Berzelius' atomic weights are all correct, the atomic heats of different elements are either equal to, or simple multiples of, one another.

(*b*) The atomic heats of all solid elements are equal; and Berzelius' atomic weights must be corrected accordingly.

They chose the latter alternative as being the simpler one, and therefore the more likely to be true. It involved dividing many of Berzelius' atomic weights by 2; in some cases a more complicated alteration was made, as will be seen from the following table of atomic weights, in which oxygen is taken as 16 (Berzelius made O = 100).

	Atomic Weight (O = 16).			
Element.	Berzelius, 1818.	Dulong and Petit, 1819.	Correction made.	Standard, 1921.
Bismuth ..	.. 284	212	÷ 4/3	208
Lead ..	.. 414	208	÷ 2	207
Gold ..	.. 398	199	÷ 2	197
Platinum ..	.. 194·5	194·5	no change	195
Tin ..	.. 235	117·5	÷ 2	119
Silver ..	.. 432·5	108	÷ 4	108
Zinc ..	.. 129	64·5	÷ 2	65·4
Tellurium	.. 129	64·5	÷ 2	127·5
Copper ..	.. 126·5	63·3	÷ 2	63·6
Nickel ..	.. 118	59·0	÷ 2	58·7
Iron ..	.. 108	54·2	÷ 2	55·8
Cobalt ..	.. 118	39·4	÷ 3	59·0
Sulphur ..	.. 32	32·2	no change	32·1

In most cases, the correction agrees with subsequent determinations, further changes in the atomic weights being accounted for by increased accuracy in the measurement of equivalent weights, and not by the introduction of any new factor. Two mistakes, however, appear in the table. Berzelius' value for cobalt should have been divided by 2, and not by 3; the error was due to an inaccurate value for the specific heat. On the other hand, his value for tellurium should have been left alone. In this case, both equivalent weight and specific heat were incorrect (Berzelius' value, though of the right order, is too high), and it so happened that the two errors compensated one another.

This empirically discovered law of atomic heats may therefore be stated as follows:

> *The product of the specific heat and the atomic weight of solid elements is approximately constant.* Taking O = 16 as standard, this constant is equal to about 6·3.

This work was extended in the years that followed by Regnault and by Kopp. Regnault's work on the accurate determination of specific heats is well known; a table of his results, given by Berzelius in 1842, contains values for the atomic weights of twenty-seven elements, determined by Dulong and Petit's law. It may be pointed out that the fact that the law is only approximately accurate does not matter in most cases, since all we need is a value of the atomic weight near enough to the truth to give us the correct whole number by which to multiply the equivalent weight, the latter being capable of accurate measurement.

Kopp's work was also based on empirical observation. He found that in very many cases *the atomic heat of an element does not change when the element enters into chemical combination.* It follows, therefore, that the product (specific heat) × (*molecular* weight) of a compound is

simply equal to the sum of all the atomic heats of the various elements in the molecule. Since the average value for the atomic heat of an element is 6·3, it follows that the molecular heat of a compound should be approximately $6{\cdot}3 \times n$, where *n* is the total number of atoms in the molecule.

Kopp was not the only investigator to assert this ; it had been stated by Neumann, in a more limited way, in 1831 ; and we shall see that Cannizzaro quotes Woestyn and Garnier in connection with this law ; but Kopp's work was so much more detailed and extensive than that of his predecessors, that the law is usually associated with his name.

Kopp's law enabled provisional values to be assigned to the atomic weights of certain elements, such as oxygen, of which the specific heat in the solid state was not known. Actually, by the time Kopp's work was published, that of Cannizzaro was also known, the latter being generally recognised as providing the most trustworthy method of finding such atomic weights. It is, however, interesting to note that Kopp was forced to distinguish between elements possessing normal atomic heats and those of which the atomic heats were definitely below normal :

(1) Elements of atomic heat approximately 6·4 (ranging from Al (5·87) to Mo (6·93)) : 39 elements, mostly metals, but including also As, Se, Te, Cl*, I.

(2) Elements of low atomic heat : C (1·8), B (2·7), Si (3·8), P (5·4), S (5·4) and also H*, O*, F*.

Limitations of Dulong and Petit's Law.—We have seen, and shall see, that in the hands of Cannizzaro this law proved of the greatest value. But it must not be forgotten that, at the time at which it was put forward, it had serious limitations, both practical and theoretical. Regarding the former, it served only to assign atomic weights to those elements of which the specific heat was

* Found indirectly from molecular heats of compounds.

known in the solid state; the vitally important atomic weights of oxygen (referred to hydrogen) and of other common non-metallic elements remained still obscure. The atomic weight of carbon was a source of great difficulty; Regnault, on grounds of atomic heat, doubled Berzelius' value, a change which Berzelius strongly resisted, since it led to the formulæ CO_2 and CO_4 for the two oxides, and greatly complicated the formulæ of organic compounds. It was not till much later that the atomic heat of this element was recognised as being definitely abnormal at ordinary temperatures (see p. 157).

It may be of interest to collect here some values which were successively assigned to carbon:

	Atomic Weight, according to		
Dalton (1810).	Berzelius (1818).	Regnault (1840).	Cannizzaro (1858).
5·4	12·2	24	12

These special difficulties apart, however, Dulong and Petit's law suffered at the time from the defect that it was entirely empirical, and that *there was no really conclusive reason why the atomic weights, obtained by its help, should not still be all in error by some constant factor.* Referring back to their original table (p. 135), it will be seen that they chose to leave the atomic weights of platinum and sulphur unchanged, and to halve most of the rest. But it might have been argued that the majority of Berzelius' values were correct, and that those of platinum and sulphur should have been doubled; or, again, that the last two should have been divided by 2, and the others by 4. These alterations would preserve Dulong and Petit's law, but would affect the numerical value of the constant. This kind of consideration was no doubt in Berzelius' mind when he wrote that "all we can do is to follow along the lines of greatest probability."

To sum up, we may say that Dulong and Petit's law, given independent confirmation, is of great value; but

that it is a *secondary* method of determining atomic weights. It needed co-ordination with the fundamental method of Cannizzaro before it could be used with confidence.

Cannizzaro used both Dulong and Petit's and Kopp's laws in a very ingenious way. Having, by the vapour density method, assigned probable values to the atomic weights of bromine and iodine, he showed that these values, multiplied by the specific heats of the respective elements, gave the products 6·75 and 6·87. This fixed the numerical value of the constant in Dulong and Petit's law as *of the order of* 6–7; *i.e.* he then showed that the atomic heat of mercury was 6·5 provided that the atomic weight of mercury were taken as 200, and *not* as 100. (Previously, many chemists had adopted 100 as the atomic weight of this metal.) He showed further that Kopp's law was fully in agreement with the value of 200. From this he proceeded to fix the atomic weights of many other metals, as we shall see in the next chapter.

The Law of Isomorphism.—The following account of crystals, and of isomorphism, is quite inadequate to a proper appreciation of the subject, for which the student is referred to a text-book of crystallography. Most of the tests of isomorphism here mentioned admit of exceptions; but to avoid confusing the beginner, they are stated as simply as possible.

Crystals are homogeneous bodies bounded by plane faces, which are arranged at definite angles with respect to one another. In certain sets of substances we find a tendency to form crystals which are very similar in shape, the angles between corresponding faces of these crystals being very nearly, if not exactly, equal. For example, a series of naturally occurring carbonates all tend to form a shape known as a rhombohedron. A rhombohedron is a six-sided figure not unlike a cube; if we take a cube, and imagine it squashed down along one diagonal (*i.e.* the line joining two opposite corners) so that the other

three diagonals remain of equal length, we obtain a rhombohedron. The extent to which the cube must be squashed in order to obtain, say, a rhombohedron of the shape of a calcite crystal, is quite definite, and may be measured by what we call the " rhombohedron angle," which is the supplement of the angle which two chosen faces of the rhombohedron make with one another. The following carbonates will be seen to have almost identical angles :

Calcite (calcium carbonate)	74° 55′
Magnesite (magnesium carbonate) ..	72° 36′
Chalybite (ferrous carbonate)	73° 0′
Calamine (zinc carbonate)	72° 20′
Rhodochrosite (manganese carbonate)	72° 58′

In addition to the similarity of angle, we find that crystals are often obtained which, though perfectly homogeneous, contain two or more of these carbonates mingled together. It is, in fact, the exception rather than the rule to obtain a pure specimen of any of the above compounds in a naturally occurring mineral. The name " mixed crystal " is sometimes given to these crystals ; it is not a very good one, as it is apt to imply that we are dealing with mixtures of crystals of different kinds. A crystal of calamine, containing magnesium carbonate or ferrous carbonate as well as the zinc salt, is however perfectly homogeneous, just as a solution of sugar in water is homogeneous. In fact, these crystals are often called *solid solutions*, a term which implies their homogeneity and variable composition.

The above set of five carbonates are said to be " isomorphous," which means *of the same shape*. Many naturally occurring minerals form isomorphous mixtures, or solid solutions ; and we meet with them also among common chemical compounds. The alums, for example, form a series of crystals which have the shape of regular octahedra—eight-sided figures, each face being an

equilateral triangle. From a mixture of two alums, perfectly homogeneous crystals may be obtained containing proportions of the two substances dependent on the proportions present in the solution. Again, if we immerse a purple crystal of chrome alum in a saturated solution of the colourless potassium aluminium alum and allow the solution to evaporate slowly, a colourless coating of the latter compound will be obtained upon the former, the whole preserving the octahedral shape. This phenomenon is known as "regular overgrowth."

Consequently we can state the following as properties possessed by isomorphous substances :

(1) They must crystallise in forms which, though they may differ slightly from one another in corresponding angles, must be very similar.

(2) They must be capable of forming homogeneous crystals containing variable proportions of the two (or more) constituents ; and these proportions must be capable of varying over wide limits.

(3) A crystal of one substance must be capable of coating a crystal of the other in a regular manner.

Though none of the above tests is by itself absolutely rigid, when all three are considered together it is seldom difficult to decide, in any particular case, whether or not two substances are isomorphous.

Mitscherlich's Law.—In 1820 Mitscherlich, Professor of Chemistry in Berlin, and a pupil of Berzelius, published a paper in which he reviewed these phenomena, and stated a general law which for our purpose may be put in the following form :

Isomorphous substances have similar chemical formulæ. According to Mitscherlich, two isomorphous substances will possess the same number of atoms in the molecule, and these atoms will be combined in the same way. We cannot illustrate this better than by taking the series of compounds examined by Berzelius when he altered the atomic weights of many of the metals. The law of

isomorphism was, indeed, invoked by Berzelius in this connection, though not exactly in the manner which follows.

Assuming it demonstrated (see above, p. 133) that sulphuric anhydride has the formula SO_3, we obtain the sequence :

Chromates and sulphates are isomorphous. Hence they have analogous formulæ ; *e.g.* if potassium sulphate is K_2SO_4, potassium chromate will be K_2CrO_4.

Hence chromic anhydride will have the formula CrO_3.

The lower oxide of chromium, chromic oxide, must therefore have the formula Cr_2O_3 (see p. 133, (*c*)).

Isomorphous with chromic salts (derived from chromic oxide) are ferric salts ; hence ferric oxide must have the formula Fe_2O_3.

Ferrous oxide must therefore be FeO.

Isomorphous with ferrous salts are many other salts—*e.g.* those of copper, zinc, nickel, etc. Hence all these salts must be derived from oxides of the general formula MO.

This is, of course, identical with the reasoning on p. 133 ; instead of the " chemically analogous behaviour " we have the law of isomorphism.

Limitations of the Law of Isomorphism.—The reader will probably perceive at once that the law stands in much the same position as Dulong and Petit's law ; it is a valuable *secondary* method of atomic weight determination. The chain of reasoning just given, for example, depends on the initial assumption that we know that sulphuric anhydride is SO_3 ; if this formula is in doubt, all the other formulæ will be uncertain in consequence. Thus all these methods—Berzelius' method of chemical analogy, the specific heat method, and the method of isomorphism—though all useful in themselves, needed some fundamental basis which should establish beyond reasonable doubt the correctness of some primary formulæ on which to hang the results of these secondary methods. It

was the absence of any fundamental co-ordination which led to such confusion during the first half of the nineteenth century, and caused some chemists almost to despair of ever finding atomic weights with certainty. From 1850–1860 the muddle was at its worst. Freund's *Study of Chemical Composition* gives an account of it :

" . . . The terms 'equivalent,' 'atomic weight,' 'molecular weight,' were used and abused in every conceivable sense ; sometimes even employed as synonymous. Lothar Meyer . . . tells how about the middle of the century HO might have stood for water or hydrogen peroxide, C_2H_2 for marsh gas or ethylene, and how in certain text-books a whole page was covered by the different formulæ assigned to and used for acetic acid."

In 1860 an international meeting was held at Karlsruhe, in order to try to obtain some kind of common agreement upon the meaning to be given to the various symbols in use at the time. At the close of the congress copies of Cannizzaro's paper were distributed. The main argument of this paper has been given in the preceding chapter ; the remainder, so far as it concerns us, will be found in the next section. Lothar Meyer said that after reading Cannizzaro, "the scales fell from my eyes, my doubts disappeared, and a feeling of tranquil security took their place" ; and so it must have seemed to many others. The period of confusion was over ; and the Periodic Table of the Elements, that great generalisation which depended for its very existence upon an accurate knowledge of atomic weights, followed only a few years afterwards.

CHAPTER XII (B)

CLEARING UP THE MUDDLE

Cannizzaro on the Atomic Weights of the Metals.—The method of finding atomic weights by determining the least weight of an element which ever enters into combination, expounded by Cannizzaro in the first part of his letter, and considered by us in Chap. XI, applies only to those elements forming compounds the molecular weights of which can be determined (in general, those elements forming gaseous or vaporisable compounds). These include all the non-metals, except the rare gases of the atmosphere; metals, on the other hand, rarely form compounds which can be vaporised without decomposition. It is desirable, therefore, to find some other method of determining their atomic weights. How this could be done was shown by Cannizzaro. We shall follow the essential lines of his treatment, though condensing it to some extent.

Dulong and Petit's Law.—In Chap. XII (A) it was shown that the product (atomic weight) $\times$ (specific heat) was apparently constant for solid elements. The value of this constant Dulong and Petit estimated at about 6·4 (O = 16). There was, however, no convincing reason why this constant might not have the value of $6{\cdot}4 \times n$, or $6{\cdot}4 \div n$, where n is a small whole number; in other words, atomic weights found by Dulong and Petit's law might still be in error by some constant factor.

Cannizzaro, however, had shown by his vapour density method that the atomic weights of bromine and iodine were probably 80 and 127 respectively (see p. 117). The

number of compounds examined was not large, but support for these figures was provided by the following considerations :

It was established beyond reasonable doubt that the atomic weight of chlorine was 35·5 (see p. 119) ; and that the molecule of hydrogen chloride contained 1 molecule of chlorine. By analogy, it would be anticipated that the very similar compounds, hydrogen bromide and hydrogen iodide, would contain one atom of the halogen element in the molecule, thus fixing the atomic weights as 80 and 127 (see Table, p. 117).

The specific heats of solid bromine and iodine were known, and the following figures are quoted by Cannizzaro :

	Atomic Weight.	Specific Heat.	Atomic Heat.
Solid Bromine ..	80	0·08432	6·74560
Iodine	127	0·05412	6·87324

This may be taken as confirming that the value of the constant in Dulong and Petit's law lies between 6 and 7, and is not any multiple or submultiple of this.

Atomic Weight of Mercury.—Data for two compounds of mercury are given in Cannizzaro's table (p. 117), namely, for calomel and corrosive sublimate. In both, the weight of mercury in a molecular weight of the compounds is 200 units ; 200 is also the molecular weight of mercury vapour. The atomic weight is therefore 200, or a simple submultiple of this. In several of the current systems of chemistry, the atomic weight of mercury was taken as 100. Cannizzaro showed, however, that the value for the specific heat of solid mercury indicated that 200 was the correct figure :

	Atomic Weight.	Specific Heat.	Atomic Heat.
Solid Mercury ..	200	0·03241	6·48200

Evidence of Kopp's Law.—Further support for the value of 200 was forthcoming from the values obtained for the molecular heats of mercury compounds. It will

be remembered that Kopp's law (actually referred to by Cannizzaro as an observation made by Woestyn and Garnier) stated that the atomic heats of the elements were not appreciably affected when the elements entered into combination. It follows, therefore, that if the specific heat of a compound be multiplied by its molecular weight, the resulting " molecular heat " should be equal approximately to $6{\cdot}4 \times n$, where n is the number of atoms in the molecule (no matter what the elements may be which compose it).

To make the procedure clear, we shall consider in detail the application of the law to mercurous chloride (calomel). The following are the relevant data :

Molecular Composition.	Specific Heat of Compound.
35·5 parts of chlorine, 200 parts of mercury.	0·05205

Empirical Formula.	Empirical Formula Weight.
(*a*) Hg = 200 : HgCl	(*a*) 235·5
(*b*) Hg = 100 : Hg_2Cl	(*b*) 235·5.

(The difference between the possible atomic weights of mercury makes, of course, no difference to the empirical formula weight ; for the purpose of this investigation, also, the *empirical* formula of the solid may be taken to be the same as the molecular formula.)

The product of 235·5 and the specific heat of calomel = 12·258. This is consequently the " molecular heat " of calomel.

(*a*) If mercury has the atomic weight of 200, the number of atoms in the " empirical molecule " of calomel = 2, and the mean atomic heat of the atoms composing the molecule is $12{\cdot}258 \div 2 = 6{\cdot}129$.

(*b*) If the atomic weight of mercury is 100, the number of atoms in the molecule of calomel = 3, and the mean atomic heat becomes $12{\cdot}258 \div 3 = 4{\cdot}086$.

It is evident that better agreement with Kopp's law

is obtained by making the atomic weight of mercury equal to 200.

(NOTE.—It is interesting, in this connection, to remark that we now consider the molecular formula of calomel to be Hg_2Cl_2 (Hg = 200). This does not affect the above reasoning; for the molecular weight of calomel then becomes 235·5 × 2. The molecular heat is thus doubled, but must then be divided by 4 instead of by 2, leaving the mean atomic heat unchanged.)

The following figures for other compounds of mercury further support Cannizzaro's conclusion:

Compound.		Molecular Heat.	Mean Atomic Heat of Elements. (*a*) Hg = 200.	(*b*) Hg = 100.
Mercurous iodide	..	12·913	6·457	4·304
Mercuric chloride	..	18·669	6·223	4·667
Mercuric iodide	..	19·054	6·351	4·763

It may therefore be taken as satisfactorily established

(i) That the value of the constant in Dulong and Petit's law is about 6·4;

(ii) That the atomic weight of mercury is 200; and

(iii) That mercury vapour is monatomic. (See Table, p. 122.)

The Atomic Weight of Copper.—From the equivalent weight of copper, analysis of its compounds, it follows that the atomic weight of copper is 63, or else a multiple or submultiple of this figure. The specific heat of copper is 0·095, whence it appears that 63 is the correct figure (which gives an atomic heat of almost exactly 6).

This was confirmed, as in the case of mercury, by examining the molecular heats of cuprous chloride and iodide, whence it became apparent that there could only be two atoms (one of copper and one of chlorine or iodine) in the empirical formulæ, which become CuCl and CuI respectively.

Atomic Weights of Other Metals.—Cannizzaro continued to apply these methods, obtaining the following results :

(a) *Atomic weight found from equivalent weight of metal and specific heat of solid metal.*

Element.	Atomic Weight.
Potassium	39
Sodium	23
Silver	108
Zinc	66
Lead	207
Iron	56
Manganese	55
Tin	117·6
Platinum	197

(b) *Value for atomic weight confirmed by applying Kopp's law to the halides of the metals.*

This was done in all the above instances.

(c) *Atomic weight found from equivalent weight of metal, and by applying Kopp's law to the chlorides (the specific heat of the solid metal not being known).*

	Atomic Weight.
Calcium	40
Magnesium	24
Barium	137

APPENDIX TO CHAPTER XII (B)

GENERAL ESTIMATE OF THE WORK OF CANNIZZARO

IT may not be out of place to summarise here very briefly the results of Cannizzaro's work.

(1) By lucid reasoning based upon Avogadro's hypothesis, Cannizzaro was able to develop a method of finding the

atomic weights of those elements which formed gaseous compounds, or compounds vaporisable without decomposition. By this means he obtained values for the atomic weights of most of the non-metals, including bromine and iodine (Chap. XI).

(2) It had already been shown, by Dulong and Petit, that the product (atomic weight) × (specific heat) for solid elements was probably constant. Cannizzaro, using solid bromine and iodine (having previously found the atomic weights of these elements by the independent method (1)), was able to show that the numerical value of the constant was about 6–7 (Chap. XII (B)).

(3) From this he proceeded to determine the atomic weights of the metals, using their specific heats in the solid state, and also applying Kopp's law to the halides of the elements (Chap. XII (B)).

(4) Method (1) is, of course, of fundamental importance, and it proved particularly valuable in that it enabled the atomic weights of many of the most important elements to be found (*e.g.* oxygen and carbon). These elements had been found to be apparent exceptions to Dulong and Petit's law, and had thus cast some doubt upon the validity of the law as a means of atomic weight determination.

(5) As has been pointed out already (pp. 138, 142), both Dulong and Petit's law and the law of isomorphism required independent confirmation, which was supplied by this work of Cannizzaro's. Henceforth they could be used with confidence as instruments for determining and confirming atomic weights.

CHAPTER XIII

THE PERIODIC TABLE

We have seen that by the year 1860 chemists were at last in possession of a means of determining atomic weights with accuracy. The principles had been established; further refinements of analysis might lead to small corrections of atomic weights, but the fear was removed that the values adopted might still prove to be in error by some factor due to some basic fault in theoretical reasoning. The results were even more far-reaching than might have been suspected; within ten years a fundamental connection was established between the chemical and physical properties of the elements and their atomic weights.

Such a connection had been indicated as early as 1829 by Döbereiner, who had selected certain "triads," or groups of three elements, which showed marked resemblance among their members. It will be sufficient to mention one such triad in detail.

Taking Berzelius' atomic weights (here expressed on the standard H = 1), Döbereiner pointed out that the atomic weights of chlorine, bromine, and iodine formed very nearly an arithmetical progression:

	Atomic Weight.	
Chlorine	35·47	Mean = 80·97; At. Wt. of Bromine = 79·38
Iodine	126·47	

He added that future more accurate determinations might show that the atomic weight of bromine was exactly equal to the mean of those of chlorine and iodine

(an example of a scientific prophecy which has *not* proved to be correct).

No further advance on these lines was made, however, until 1863 and the years immediately following, when Newlands, an English chemist, published a series of papers in the *Chemical News*, in which he maintained that if the elements were arranged in the order of their atomic weights, " the 8th element starting from a given one is a kind of repetition of the first."

In order to maintain the regularity of the relationship, Newlands was obliged occasionally to group two elements together and to transpose others. Jugglery of this kind, combined with the fact that not much resemblance could be traced between certain of the elements in the horizontal series, led to much criticism of the " Law of Octaves," as Newlands christened his discovery. One member of the Chemical Society, at a meeting held in 1866, suggested that any arrangement of the elements would show chance resemblances here and there ; and he asked Newlands if he had ever tried arranging the elements in alphabetical order.

It is now realised, however, that Newlands was on the track of a great discovery. The credit of establishing beyond doubt that there is a " periodic " relationship between atomic weights and the properties of the elements must nevertheless be given to Lothar Meyer and Mendeléeff. A complete discussion of their work would take us far too long ; an account of Lothar Meyer's " Atomic Volume " curve, and of Mendeléeff's Periodic Table will be found in all text-books of Inorganic Chemistry. We must concern ourselves here merely with such aspects of the Periodic Table as have influenced atomic weight determinations.

In Mendeléeff's table, in which similar elements were grouped in vertical columns, there were a number of blank spaces. These were deliberately left, in order to preserve the general classification ; and Mendeléeff

expressed the firm belief that elements would later be discovered which would fill these spaces. A portion of his table is reproduced below, to make this clear.

Li=7	Be=9·4	B=11	C=12	N=14	O=16
	Mg=24	Al=27	Si=28	P=31	
	Ca=40	—	Ti=48	V=51	
	Zn=65	—	—	As=75	
	Cd=112	In=113	Sn=118	Sb=122	

From its physical and chemical properties, arsenic should evidently lie between phosphorus and antimony in the *vertical* series. Hence Mendeléeff predicted that two elements would be found, of atomic weights 68 and 72, which would lie between zinc and arsenic in the horizontal series; and, on similar grounds, that an element would be found, of atomic weight 44, which would fill the blank space between calcium and titanium. These elements he called eka-aluminium, eka-silicon, and eka-boron respectively; and he predicted not only their atomic weights, but many of their physical and chemical properties. These prophecies were strikingly fulfilled, as is shown below:

	Atomic Weight. (predicted).	Atomic Weight. (found).	Present Name.	Discovered.
eka-aluminium	68	70	Gallium	1875
eka-silicon ..	72	72·5	Germanium	1886
eka-boron ..	44	45	Scandium	1879

The Periodic Law, expressed in the form "The physical and chemical properties of the elements are periodic functions of their atomic weights," is of course recognised by now as one of the most fundamental generalisations in chemical science. It gives, in itself, the strongest possible confirmation of the correctness of our present atomic weights, since any alteration of a given atomic weight, beyond a slight correction, would derange the whole classification. Further, by leaving only a few

blank spaces to be filled, it tells us at once the approximate atomic weights of the elements which must fill them. Since the equivalent weight of any element can be determined with accuracy, and all we require to know is by what whole number the equivalent weight must be multiplied in order to give the accurate atomic weight, the importance of the Periodic Classification as an instrument in helping to decide doubtful cases is evident.

Nevertheless, the Periodic Table had first to be established. If the atomic weights of many elements had not previously been determined by the methods described in earlier chapters of this book, the table itself could not have been constructed, and the periodic law would have remained unknown. Hence, from this point of view, the Periodic Classification must be regarded as a secondary method of atomic weight determination ; and, whatever its significance may be in other respects, in this it stands much on the same footing as Dulong and Petit's Law and the Law of Isomorphism.

Reference may be made here to certain " anomalies " in the Periodic Table, which until recently were the source of much inconclusive speculation. There are three principal cases in which the placing of the elements in order of increasing atomic weight leads to a grouping which is obviously not in accordance with other physical and chemical properties. These are the pairs of elements nickel and cobalt ; tellurium and iodine ; and argon and potassium. The last of these will be considered in Chap. XV.

Nickel and Cobalt.—Iron forms two well-marked series of salts, in which the valencies of the metal are 2 and 3. Cobalt likewise exerts valencies of 2 and 3, though cobaltic salts, with the exception of certain complex salts, are unstable. Nickel is uniformly divalent.

There is no doubt that when the physical and chemical properties of these " transition metals " are considered, cobalt should be placed between iron and nickel. This

is not, however, in agreement with the atomic weight sequence, which is as follows:

	Atomic Weight 1921. (O = 16).
Iron	55·84
Nickel	58·68
Cobalt	58·97

The following quotation is taken from Chap. V of *The Theory of Valency*, by Dr. J. Newton Friend (1909 edition), written at a time when these anomalies had not yet met with a solution:

" . . . The atomic weight of nickel, as determined in a variety of ways by a number of careful investigators, is always found to be slightly less than that of cobalt. Krüss and Schmidt thought that this was due to the presence of a hitherto undiscovered element, to which they gave the name *gnomium*. . . .

" During the past few years, Richards, Baxter, and others have been determining the atomic weights of nickel and cobalt afresh, but as yet the difficulty has not met with solution."

Tellurium and Iodine.—From their physical and chemical properties there can be no doubt (*a*) that iodine should be placed in the halogen family, with fluorine, chlorine, and bromine; and (*b*) that tellurium is the higher homologue of selenium in Group VI. Tellurium should therefore lie between antimony (atomic weight 120·2) and iodine (126·92). The value for the atomic weight of tellurium now accepted is, however, 127·5.

There were many attempts in the early years of this century to explain this anomaly. Baker and Bennett (*Trans. Chem. Soc.*, **91**, 1849 (1907)) published an elaborate research upon the atomic weight of tellurium, using specimens of the element obtained from Bohemia, Australia, South America, and Japan. By seven different methods, including fractional distillation of the element

and of its dioxide and tetrachloride, fractional crystallisation of barium tellurate, fractional decomposition of the hydride, and fractional electrolysis of the tetrachloride and tetrabromide, these workers attempted to discover if tellurium could be separated into two or more elements. The atomic weight of the tellurium was determined by analysis of the various fractions obtained in the above processes, but no difference between extreme fractions could be detected. The mean of forty-three determinations gave 127·6 as the atomic weight.

Further attempts to show that tellurium contained some other element proved abortive, and Friend (*loc. cit.*) added, after examining the evidence available :

"The last twenty years, therefore, do not seem to have brought us a single stage nearer to the solution of the difficulty, and for the present tellurium must be regarded as an exception to the Periodic Law."

The explanation followed not long afterwards, as the result of physical investigation into the nature of the atom. These results will be considered in Chap. XXI.

The Periodic Table has been used to correct the values previously adopted for the atomic weights of certain elements. Examples will be found in the next chapter.

References

Extracts from Mendeléeff's work will be found in Whetham's *Cambridge Readings* (see reference at end of Chap. IX).

Most of the larger text-books of Inorganic Chemistry give an account of the Periodic Table ; books dealing especially with this subject are :

Systematic Inorganic Chemistry, by Caven and Lander.

The Foundations of Chemical Theory, by Caven ; and *Atoms and Molecules*, being Part I and Chap. XII of *The Foundations of Chemical Theory*.

(All three published by Blackie & Son, Ltd. ; prices 9*s*., 12*s*. 6*d*., and 7*s*. respectively.)

Exercises on Chapter XIII

Write an essay upon the following subject:

"The Establishment by Induction of the Law that 'The Physical and Chemical Properties of the Elements are Periodic Functions of their Atomic Weights.'"

Note.—It is suggested that you illustrate the three main steps characteristic of induction (Chap. I, p. 4).

1. *Collection of relevant facts.*—Of the vast mass of material possible to take in this connection, the following may be selected:

Lothar Meyer's curve of atomic volumes.

General properties of the oxides and chlorides of the elements.

(Much more may, of course, be taken, if desired: *e.g.* other physical properties, and general "electrochemical" character of the elements.)

2. *Framing the hypothesis.*—The hypothesis has been stated above, as a "law"; in science there are many examples of statements which may be regarded as being at one time hypotheses, and which have now obtained such general confirmation that they have been raised to the dignity of laws. It is not proposed here to insist too narrowly upon a distinction between the two terms; the student should, however, bear in mind the *general* distinctions between facts, laws, and hypotheses made in Chap. I.

3. *Testing the Hypothesis.*—This may be illustrated in two chief ways: (*a*) the prophecies of Mendeléeff regarding the "eka" elements, and their confirmation; (*b*) the correction of the atomic weights of beryllium, etc. (see next chapter).

All the material for the above essay, if not already known to the student, can be found in any moderate-sized text-book of Inorganic Chemistry.

CHAPTER XIV

SOME INTERESTING ATOMIC WEIGHTS

Carbon.—It has already been shown that the atomic weight of this element was for some time a source of controversy; and different values for the atomic weight, reached by various investigators, have been given above (p. 138). Regnault obtained the value of 0·2411 for the specific heat of carbon, which gave, by the application to it of Dulong and Petit's law, the approximate value of 26 for the atomic weight. Regnault, therefore, proposed to double the value of 12 which had been previously assigned to the element by Berzelius, an alteration which Berzelius strongly resisted. During the years that followed, various values for the atomic weight were adopted, with consequent confusion in the realm of organic chemistry. The matter was, of course, settled by Cannizzaro, who showed that the weights of carbon in molecular weights of its compounds were always multiples of 12 (see above, p. 123).

If, however, we accept 12 as the atomic weight of carbon, we must admit that this element forms an exception to Dulong and Petit's law, since the product $12 \times 0{\cdot}24$ is only 2·9. This anomaly was investigated by Weber (1875). Weber pointed out that Regnault himself obtained different values for the specific heat of graphite and diamond, and that a number of subsequent workers obtained results differing from those of Regnault and from each other's. He decided that

"the differences in the individual results are so great and so general as to preclude us from believing that they are due to errors in the methods of experiment, or to impurities in the substances themselves."

From an examination of the results, Weber showed that the probable cause of divergence lay in the fact that different experimenters had taken different temperature intervals in measuring the specific heat. Some of the results were as follows :

	Temperature Range.	Mean Temp.	Specific Heat.	
Diamond ..	6°–15° C.	10·5°	0·1192	(1)
	24°–70° C.	47°	0·1429	(2)
	9°–98° C.	53·5°	0·1469	(3)
Graphite ..	21°–52° C.	36·5°	0·174	(4)
	24°–67° C.	45·5°	0·1881	(2)
	17°–99° C.	58°	0·1977	(3)

The result numbered (1) was due to de la Rive and Marcet, those numbered (2) to Wüllner and Bettendorf, those numbered (3) to Regnault, and that numbered (4) to Kopp.

They indicate strongly that the specific heat of carbon rises with increase of temperature. Weber proceeded to verify this. He obtained for his experiments the loan of the entire diamond collection of the University of Berlin, the total weight of the diamonds employed being 3·562 grms. These he used at moderate temperatures (up to 282 degrees C.). For experiments at higher temperatures less valuable diamonds from the Imperial Mineral Cabinet in Vienna were used, weighing again over 3 grms. He used a straightforward calorimetric method, comparing the heat given out on cooling a weighed quantity of diamond with that given out by a piece of platinum of approximately equal heat capacity. From the latter he calculated the temperature of the muffle furnace in which both diamonds and platinum were heated, and thence found the mean specific heat of the diamond over the given temperature range in the usual way.

The results showed quite definitely that the specific heat of carbon in this form rose with increase of tempera-

ture. Some of the figures calculated from the experimental results were as follows :

Temperature (°C.).	Specific Heat.	Sp. Ht. × 12.
— 50·5	0·0635	0·76
+ 10·7	0·1128	1·35
140	0·2218	2·68
247	0·3026	3·64
615·2	0·4438	5·32
986·8	0·4622	5·55

At high temperatures, therefore, it appeared that the atomic heat tended towards the normal value of about 6.

Similar results were obtained for graphite ; the specific heat of this allotropic form was greater, at ordinary temperatures, than that of diamond, but it did not rise so rapidly with increase of temperature, so that the limiting value at high temperatures appeared to be about the same.

Boron and Silicon.—The specific heats of these elements were also investigated by Weber. A number of volatile compounds of both elements had been examined, though not, of course, so many as in the case of carbon. The atomic weights found by this method appeared to be B = 11, Si = 28. Calculated from Dulong and Petit's law, however, using the specific heats at normal temperatures, the atomic weights were approximately 27 and 38 respectively. Weber showed that, as with carbon, the specific heat rose as the temperature increased, tending at high temperatures towards normal values.

Boron (a crystalline specimen, obtained by reducing boric acid with aluminium).

Temperature (°C.).	Specific Heat.	Sp. Ht. × 11.
— 39·6	0·1915	2·11
+ 26·6	0·2382	2·62
125·8	0·3069	3·38
233·2	0·3663	4·02

Silicon (crystalline; obtained by reducing calcium silicofluoride with zinc and sodium).

Temperature (°C.).	Specific Heat.	Sp. Ht. × 28.
−39·8	0·1360	3·81
+21·6	0·1697	4·75
128	0·1964	5·50
232·4	0·2029	5·68

Weber added, as a comment on the results obtained with silicon, that "it also follows that the smallest relative weight of silicon (28) hitherto found in the molecule of any of the gaseous compounds of this element is in reality the atomic weight of silicon."

No further doubt, therefore, remained regarding the atomic weights of these three elements. Later work has shown that the specific heats of all elements fall as the temperature is lowered; for most elements, however, the drop in the specific heat does not become marked until very low temperatures are reached. Carbon, boron, and silicon are therefore only exceptional in that the maximum value of the atomic heat is not reached except at relatively high temperatures.

Vanadium.—This offers an interesting example of the correction of an atomic weight by the application of the Law of Isomorphism.

A value for the atomic weight of vanadium had been given by Berzelius, who had demonstrated the following facts:

(*a*) Vanadic anhydride, on heating to redness in hydrogen, leaves a lower oxide;

(*b*) this lower oxide, on heating in chlorine, gives a volatile chlorine compound, and a residue of vanadic anhydride exactly equal in weight to one-third of that of the vanadic anhydride originally taken for reduction.

These results he explained essentially as follows (the formulæ of the molecules of hydrogen, chlorine, and

water have been corrected, as the argument is not thereby affected) :

$$(a)\ 3VO_3 + 6H_2 = 3VO + 6H_2O.$$
$$(b)\ 3VO + 3Cl_2 = VO_3 + 2VCl_3.$$

Hence three molecules of vanadic anhydride originally taken yield eventually one molecule of the anhydride.

In 1867, however, Sir Henry Roscoe published his "Researches on Vanadium" (*Proc. Roy. Soc.*), in which he showed that Berzelius was in error. This work was based on the isomorphism of the minerals apatite, pyromorphite, mimetite, and vanadinite. These minerals crystallise in the hexagonal system, and frequently form isomorphous mixtures with one another. The first three have the following constitution :

Apatite (fluophosphate of calcium), $(CaF)Ca_4(PO_4)_3$,
Pyromorphite (chlorophosphate of lead), $(PbCl)Pb_4(PO_4)_3$,
Mimetite (chloroarsenate of lead), $(PbCl)Pb_4(AsO_4)_3$.

That is to say, they may be regarded as essentially derivatives of orthophosphoric and orthoarsenic acids.

Now, vanadinite, isomorphous with these minerals, is a chlorovanadate of lead ; and, according to the law of isomorphism, its formula should be analogous to those of apatite, etc., namely

$$(PbCl)Pb_4(VO_4)_3\ ;$$

the formulæ of vanadic acid being H_3VO_4, and that of vanadic anhydride V_2O_5.

Roscoe, therefore, explained Berzelius' results by the following equations :

$$(a)\ 3V_2O_5 + 6H_2 = 3V_2O_3 + 6H_2O.$$
$$(b)\ 3V_2O_3 + 6Cl_2 = V_2O_5 + 4VOCl_3.$$

As before, one molecule of vanadic anhydride is eventually obtained from three originally taken ; but the valencies

of vanadium become 5 and 3, by analogy with those of phosphorus and arsenic.

The atomic weight given by Berzelius was 68·5; Roscoe (who repeated Berzelius' experiment with greater accuracy) found the corrected value to be 51·36.

Beryllium.—The equivalent weight of this element was found to be 4·7. There were various reasons for regarding the element as trivalent, the principal being the following:

Specific heat = 0·4. Whence, by Dulong and Petit's law, approximate atomic weight = 16, which is approx. 4·7 × 3.

Resemblance to Aluminium.—Beryllium oxide is amphoteric. After strong ignition, it is insoluble in acids. The metal itself is not attacked by nitric acid.

In these respects, beryllium resembles aluminium, and differs from most of the divalent metals, such as magnesium. Nevertheless, Mendeléeff considered that the metal was probably divalent. To make his argument clear, let us consider the "first short series" in the Periodic Table:

Li		B	C	N	O	F
7	—	11	12	14	16	19

If beryllium be trivalent, its atomic weight will be 14·1; if divalent, 9·4. Mendeléeff pointed out that the latter value would place the element between lithium and boron; the former would require it to be in a position "for which no place could be found in the periodic system." He supported his argument by certain chemical considerations; but the matter was settled by a determination by Nilson and Pettersson of the vapour density of beryllium chloride. The weight of beryllium present in a gram-molecular weight of this compound was found to be 9 grms., a fact which fixes the *maximum* atomic weight of beryllium as 9.

The value at present adopted for the atomic weight is 9·1. It was shown by Humpidge (*Proc. Roy. Soc.*, 1880) that the specific heat of beryllium increases with rise of temperature :

Temperature (°C.).	Specific Heat.	Sp. Ht. × 9·1.
0	0·3756	3·42
200	0·5420	4·93
500	0·6206	5·65

The above instance, therefore, may be taken as an example in which the Periodic Law was applied in the first place to the correction of an erroneous value for the atomic weight of an element. Other examples were the correction of the atomic weights of indium and uranium. In the case of indium, the correction made was supported by a subsequent determination of the specific heat ; in that of uranium, by a determination of the vapour densities of the volatile chloride and bromide.

Exercise on Chapter XIV

Roscoe found, as the mean of four experiments, that 24·556 grms. of vanadic anhydride, on reduction in hydrogen, gave 20·256 grms. of the lower oxide.

Calculate the atomic weight of vanadium (*a*) on Berzelius' view regarding the reaction ; (*b*) on Roscoe's view (taking O = 16).

The specific heat of vanadium is 0·115. Which of the two views is corroborated by this fact ?

CHAPTER XV

THE KINETIC THEORY OF GASES, AND ITS BEARING UPON THE DETERMINATION OF ATOMICITY

THE subject-matter of this chapter takes us into regions which demand some knowledge of elementary mechanics. The reader who has not this knowledge is advised to omit pp. 169–178, and the appendix (pp. 186–190); in the remainder of the chapter, the fundamental assumptions underlying the simple kinetic theory are given, together with some of the results which can be deduced mathematically from them.

The Simple Gas Laws.—We shall begin by considering the experimentally established laws connecting the volume of a gas with its pressure and temperature. These are :

(1) *Boyle's Law.*—The volume occupied by a given mass of any gas is inversely proportional to the pressure upon it, provided the temperature be kept constant. (For example, if we double the pressure, the volume will be halved.) This may be written in the form

$$p \times v = \text{constant} \quad . \quad . \quad . \quad (1)$$

(2) *Charles's Law.*—The volume occupied by a given mass of any gas is directly proportional to its absolute temperature, provided the pressure be kept constant. The absolute temperature is obtained by adding 273 to the Centigrade temperature ; thus, if t be the Centigrade temperature, Charles's law states that

$$v = k(t + 273), \text{ where } k \text{ is a constant.}$$

Writing T for the absolute temperature, we obtain

$$v = kT \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Equations (1) and (2) may be combined into a single equation. For a given mass of any gas, this equation is

$$pv = KT \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

where K is a constant depending upon the quantity of gas which is taken. If $T =$ constant, equation (1) is obtained; if $p =$ constant, we obtain equation (2).

The usefulness of this combined equation becomes very much greater if we include in it a consequence of Avogadro's hypothesis. It is easily seen that we may alter the wording of this hypothesis to read, "Considering gases measured under equal conditions of temperature and pressure, equal numbers of molecules will occupy equal volumes."

Gram-molecular weights of all substances must contain equal numbers of molecules, since the gram-molecular weight is by definition directly proportional to the molecular weight. Hence, *gram-molecular weights of all gases, measured at the same temperature and pressure, occupy the same volume.*

Suppose we have gram-molecular weights of two gases, A and B; then for each gas

$$P_A V_A = K_A T_A$$
$$P_B V_B = K_B T_B$$

where P, V, and T are the pressures, volumes, and absolute temperatures of the respective gases. When $P_A = P_B$, and $T_A = T_B$, it follows from the above statement in italics that $V_A = V_B$.

Hence, $K_A = K_B$; and we obtain the very important result that when gram-molecular weights of gases are considered, the value of the constant is independent of

the particular gas. We can, therefore, write the general equation

$$PV = RT \quad . \quad . \quad . \quad . \quad (3)$$

where R is a constant which has the same value for all gases, provided gram-molecular weights are considered.

At "Normal Temperature and Pressure," $P = 1$ atmosphere, $T = 273$, and V is found to be 22·4 litres. This is the well-known "gram-molecular volume." The student must, of course, beware of statements such as "the product RT equals 22·4 litres"; the product RT is equal to 22·4 *litre-atmospheres*, which is a very different matter. It may readily be shown, by applying the method of dimensions, that R has the dimensions of energy divided by temperature; the value of R may be expressed in any energy units; it is found to be equal to

83·15 ergs per degree,
or 1·9885 calories per degree.

R is usually called the "Gas Constant."

The laws, then, which govern the volumes of gases with respect to pressure and temperature are vastly more simple than those determining such relationships in the case of liquids and solids. Liquids and solids have *characteristic* coefficients of thermal expansion and compressibility, which are very much smaller than those of gases.

The fundamental explanation of this difference, from the standpoint of molecular theory, has been pointed out in Chap. IX; it is due to the fact that the molecules of liquids and solids are sufficiently close together to allow of the operation between them of forces of cohesion. These cohesive forces vary for different molecules, and also vary in a complex manner with the temperature. With gases, on the other hand, the molecules are so far apart, compared with their actual sizes, that the effect of attractive forces between them may be neglected.

The Kinetic Theory of Gases.—No gas obeys the simple gas laws with complete accuracy. For example, Charles's law would require that the volume occupied by any mass of gas, however great, would become zero at 0 degrees absolute. Actually, all gases liquefy before this temperature is reached. In the account which follows, such deviations from the gas laws will be disregarded, and we shall imagine that we are dealing with an "ideal gas," which obeys the laws perfectly. The simple kinetic theory has been modified, more or less successfully, to deal with the phenomenon of liquefaction (for example, van der Waals' famous theory takes account of the attractive forces between the molecules, and of their finite volume). Such elaborations do not, however, concern us.

We have seen Dalton's picture of a gas (p. 84). For many reasons, this picture has proved to be inadequate, and the ideal gas is supposed to consist of molecules having the following properties :

(1) The molecules have mass, but are of a size negligible compared with the distances between them. (They may be regarded, in fact, as "heavy points.")

(2) They are in constant motion ; consequently they will be continually colliding with one another, and with the walls of the vessel which contains the gas. (In the simple theory, collisions between the molecules themselves are disregarded.)

(3) All collisions which they make are perfectly elastic.

The meaning of a "perfectly elastic collision" is not difficult to grasp. Suppose we drop a lump of lead on to the floor. It shows no tendency to rebound. At the moment of striking the floor, it had kinetic energy. (In mechanical theory, anything which can do work is said to possess energy. One of the ways in which a body can possess energy is by being in motion. Energy due to motion is called kinetic energy ; and this is the only kind of energy with which the simple theory of gases is

concerned.) Now, what happens to the kinetic energy possessed by the lead ? Those who have heard of the Conservation of Energy will know that it is not lost, but changed into some other form or forms. A small portion of it appears as sound energy, producing a thud. Most of it, however, is changed into heat energy, the temperature of the lead rising slightly after its collision with the floor.

This is an example of an inelastic collision. If now we drop a golf-ball on to a hard floor, it will rebound; not, indeed, to its former height, but to within a respectable fraction of that height. This is a comparatively elastic collision ; some of the kinetic energy the ball possessed when it struck the floor has been changed, as before, into sound and heat energy, but much of it remains as kinetic energy (we disregard the moment during which the ball is stationary, and slightly distorted, on the floor) ; and the ball starts to rise from the floor with a velocity nearly equal to that which it had at the moment of striking.

If the golf-ball were in a vacuum, so that there were no resistance offered to it by the air, and if it had made a perfectly elastic collision with the floor, it would have risen to precisely its former height. It requires little imagination to see that it would go on bouncing for ever. Now this is precisely what gas molecules do. They are constantly bombarding the walls of the vessel (all the walls, not only the bottom) and making perfectly elastic collisions with them. If our senses were sufficiently fine, we should be able to feel, if we grasped a penny balloon, this bombardment as a series of little blows ; but there are so many blows per second, and each is so small, that all we feel is a uniform pressure.

We can easily deduce what would happen if the molecules were not perfectly elastic. The molecules would gradually slacken speed, and finally stop. Hence the pressure of the gas would gradually fall to zero. This is not what actually occurs ; the balloon, provided it

does not leak, remains blown out. Hence the collisions must be perfectly elastic.

We can also see, in a general way, that the force exerted by the gas on a square centimetre of wall surface will, at a given temperature, be directly proportional to the number of blows on it per second. This in turn will be directly proportional to the concentration of the molecules in the gas. Hence we reach the result that the pressure exerted by a gas at a given temperature will be directly proportional to the concentration of the gas ; *i.e.* inversely proportional to its volume, which is Boyle's law. This deduction was made as long ago as 1738 by Bernouilli.

These general conceptions may be rendered more precise by the application to them of mechanical principles ; that is, by supposing the molecules to obey the laws which have been found to obtain for larger bodies.

Consider a cube, of side l cm., and suppose a molecule, of mass m, to be moving perpendicularly towards one face of the cube with a velocity of x centimetres per second On arriving at the wall, it will deal it a blow, moving away immediately afterwards with the same velocity of x cm./sec. The momentum of the molecule is equal to the product of the mass and the velocity, that is, equal to mx. But momentum has direction as well as magnitude. Hence, if we say that the molecule before arriving at the wall has a momentum of $+mx$, after collision with the wall its momentum will be $-mx$. The *change of momentum* on collision is therefore

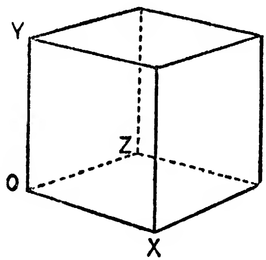

FIG. 3.

$$+mx - (-mx) = 2mx.$$

The force which is exerted on the wall by the molecule is due to these collisions. It is a theorem in mechanics that force can be measured by the *rate of change of momentum*. In

order to apply this theorem to this particular case, we have to consider the number of impacts which the molecule makes with the walls in one second.

Consider two opposite faces of the cube; and suppose that the molecule is moving to and fro between these faces with the uniform velocity x cm./sec. Since the distance between the two faces is l cm., it will strike *one* of the opposing faces x/l times per second. Every time it does this, it suffers a change of momentum equal to $2mx$; so that the *change of momentum per second* undergone by the molecule is equal to

$$2mx \times \frac{x}{l} = \frac{2mx^2}{l},$$

and this will be *the force on the two opposing walls exerted by the molecule.*

If there are n molecules in the cube, all behaving in the same way, the total force exerted by them on the walls will be

$$\frac{2nmx^2}{l}.$$

Actually, of course, the molecules will not all be moving perpendicularly to two of the faces; they will be moving in all possible directions. We can take account of this in a very simple way. It is an elementary conception in mechanics that a given velocity can always be resolved along two axes at right angles to one another. If v be the velocity, and x and y its components along the two axes, then

$$v^2 = x^2 + y^2.$$

In the case under consideration the molecules are moving about in space, and their velocities must be resolved along the *three* mutually rectangular axes, OX, OY and OZ. If c be the velocity of the molecule, and x, y and z the components of this velocity along the three axes, we have, as before,

$$c^2 = x^2 + y^2 + z^2.$$

c is here known as the "Root Mean Square Velocity" of the molecule. It is not quite the same as the average velocity of the molecules, but is near enough to it for our purpose.

Returning for a moment to the solitary molecule, which we now imagine to be moving with root mean square velocity c in any direction, we see that the total force it exerts on all the faces of the cube will be

$$\frac{2m}{l}(x^2 + y^2 + z^2) = \frac{2mc^2}{l}.$$

The n molecules present in the cube will, therefore, exert a total force of

$$\frac{2nmc^2}{l}.$$

Now *pressure* = *force per unit area.* The area of all six faces of the cube is $6l^2$ sq. cm.

Hence the pressure on the walls will be

$$\frac{2nmc^2}{l} \div 6l^2 = \frac{1}{3}\frac{nmc^2}{l^3}.$$

But $l^3 = v$, the volume of the cube. Therefore p, the pressure, is given by

$$p = \frac{1}{3}\frac{nmc^2}{v}\text{; and } pv = \tfrac{1}{3}nmc^2.$$

If we consider a gram-molecule of the gas, $n = \text{N}$, which is "Avogadro's Number," *i.e.* the number of molecules in a gram-molecular weight of any substance.

So, finally

$$\text{PV} = \tfrac{1}{3}\text{N}mc^2 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

No allowance has been made in this deduction for the effect of intermolecular collisions.

Deductions from Equation (4).—From this equation we can proceed to draw some important conclusions. In the first place, *if the temperature be kept constant*, we know that PV = constant. Hence the R.H.S. of (4) is also constant. N is constant, and m is constant; hence c is constant, and the root mean square velocity (and the average velocity) of the molecules remains constant at a given temperature.

The kinetic energy of a molecule moving with velocity c is $\frac{1}{2}mc^2$. The total kinetic energy of the N molecules present will be $\frac{1}{2}Nmc^2$. Let us denote this by E. We can, therefore, write equation (4) in the form

$$PV = \tfrac{2}{3}E \quad . \quad . \quad . \quad . \quad . \quad (5)$$

It follows from Boyle's law that *the total kinetic energy of the molecules of an ideal gas remains constant, provided the temperature does not alter*; and hence *at constant temperature the average kinetic energy of the molecules of an ideal gas is constant.*

Combination with Charles's Law.—Equation (3) states that

$$PV = RT.$$

Combining this with equation (5), we obtain

$$E = kT \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where k is a constant.

Hence *the kinetic energy of the molecules of an ideal gas is proportional to the absolute temperature.* This gives us a valuable conception of temperature in terms of energy. Numerically, k in the above equation is equal to $\frac{3}{2}R$; hence

$$E = \tfrac{3}{2}RT \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Combination with Avogadro's Hypothesis: Two Gases in Equilibrium.—Let us now consider two gases, A and B, at pressures p_A and p_B respectively, occupying volumes v_A and v_B. Let n_A and n_B be the numbers of molecules of each gas present, and m_A and m_B the masses of the molecules. We have, from the equation immediately preceding (4),

$$p_A v_A = \tfrac{1}{3}n_A m_A c_A{}^2$$

and

$$p_B v_B = \tfrac{1}{3}n_B m_B c_B{}^2,$$

where c_A, c_B are the respective root mean square velocities of the molecules of A and B.

Suppose now that we are dealing with equal volumes of the two gases, measured at the same temperature and pressure. Then

$$p_A = p_B\text{; and } v_A = v_B.$$

Further, by Avogadro's hypothesis,

$$n_A = n_B.$$

From the equality of p_A and p_B, and of v_A and v_B, it follows that

$$n_A m_A c_A^2 = n_B m_B c_B^2\ ;$$

and since $n_A = n_B$,

$$\tfrac{1}{2}m_A c_A^2 = \tfrac{1}{2}m_B c_B^2.$$

Hence, *with two gases at the same pressure and temperature, the average kinetic energies of their molecules will be equal.*

Converse of the above Deductions.—The writer is well aware that in many, if not most, books dealing with the elementary kinetic theory, these deductions are usually given in the reverse order. It should be readily seen that if we make the following assumptions :

(*a*) The average kinetic energy of the molecules of an ideal gas is constant at a given temperature ;

(*b*) When two gases are in equilibrium, that is, are at the same pressure and temperature, the average kinetic energies of their molecules are equal ;

then Boyle's law will follow from (*a*), and Avogadro's hypothesis from (*b*).* If we make the further assumption that

(*c*) The average kinetic energy of the molecules of a gas is directly proportional to the absolute temperature,

then Charles's law follows from this.

Assumptions (*a*) and (*b*) are frequently made, and are sometimes described as " fundamental theorems in mechanics." The student is thus led to believe that Avogadro's hypothesis may be deduced " independently " by means of the kinetic theory. A full discussion of this would be out of the question here ; but the following remarks may be made.

" *Classical Mechanics*."—This is a system of mechanics which has been based upon observation of bodies sufficiently large to be weighed, measured, and have their motion

* These deductions will be found as an exercise at the end of this chapter.

directly recorded. Based on the work of many observers, chief among whom was Newton, it has proved adequate to deal with most of the phenomena studied by physicists until quite recent years. It is one of the basic principles of this system that equilibrium between two sets of moving particles can only exist when the average kinetic energies of the particles are equal. It is doubtful, however, whether such a principle can be regarded as established beyond doubt. Thus, James Walker (*Introduction to Physical Chemistry*) says, in discussing the kinetic theory:

> "We learn that systems of moving particles, such as gases, are supposed to be on the assumptions of the kinetic theory, are in equilibrium with each other when the mean kinetic energies of their particles are equal;"

but he adds, in a footnote:

> "The validity of this statement is disputed by some physicists."

In the writer's opinion, one is on much firmer ground in taking the simple gas laws and Avogadro's hypothesis as established by an overwhelming mass of experimental evidence, and in arguing on the lines given above. Such a course would seem especially advisable, in view of the recent developments of atomic and molecular physics, from which it appears that many of the simple assumptions of classical mechanics are inadequate to deal with such very small particles. Until recently there was no reason to suppose that bodies of atomic dimensions would not behave like comparatively large bodies; but there is now strong evidence that they do not so behave.

Application of the Kinetic Theory to Specific Heats of Gases.—We will define the term "molecular heat of a gas" as the number of calories of heat required to raise the temperature of a gram-molecule of gas through one degree Centigrade. In the case of gases, it is necessary to state whether, during the raising of the temperature, the gas is kept at constant volume or at constant pressure. The reason for this is that in the latter case the gas will expand against the external pressure, and so will do work. In order to do work, energy must be supplied to it, in the form of heat. Hence the molecular

heat of a gas will be greater at constant pressure than at constant volume.

Consider first the molecular heat at constant volume. At T° Abs. a gram-molecule of gas will possess energy equal to $\frac{3}{2}RT$ (equation (7)). When its temperature has been raised to $T + 1$ degrees, the energy of the gas (which is due entirely to the kinetic energy of its molecules) will be $\frac{3}{2}R(T + 1)$. The difference between these two quantities of energy will be the molecular heat at constant volume (C_v). Thus:

$$C_v = \frac{3}{2}R(T + 1) - \frac{3}{2}RT = \frac{3}{2}R \quad . \quad . \quad (8)$$

More elegantly,

$$C_v = \left(\frac{\delta E}{\delta T}\right)_v = \frac{\delta}{\delta T}\left(\frac{3}{2}RT\right)_v = \frac{3}{2}R.$$

Suppose now that the gas is kept at constant pressure. In raising its temperature 1 degree, the kinetic energy of the molecules undergoes precisely the same increase as before. In addition, however, work is done on expansion. This work is equal to

$$P(V_2 - V_1),$$

where V_1 = the volume of the gas at T degrees, and V_2 = the volume at $T + 1$ degrees. But, since $PV = RT$,

$$P(V_2 - V_1) = R(T + 1 - T) = R.$$

Hence, the molecular heat at constant pressure (C_p) is given by

$$C_p = C_v + R = \frac{3}{2}R + R = \frac{5}{2}R \quad . \quad . \quad (9)$$

Monatomic Gases.—These values for C_p and C_v have been deduced on the assumption that the gas is an "ideal" one. In such a gas, all the energy of the molecules is *kinetic energy of translation*, that is, kinetic energy which they possess by virtue of their moving from one position to another. The molecule is not supposed to possess any *internal* energy.

A molecule possessing only kinetic energy of translation may be regarded either as a heavy point or as a perfectly smooth sphere (the significance of this will be clearer later on). With a gas composed of such molecules, C_v and C_p

should have the values given by equations (8) and (9), and the ratio of the two will be given by

$$\frac{C_p}{C_v} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1 \cdot 667 \quad . \quad . \quad . \quad . \quad (10)$$

This will also evidently be equal to the ratio of the specific heats of the gas at constant pressure and constant volume, since molecular heat = specific heat × molecular weight, the molecular weight cancelling out.

It is naturally of the greatest interest to see if any gases do give this value. The most convenient method of finding the ratio C_p/C_v (which we will in future denote by the symbol γ) is by the measurement of the velocity of sound in the gas. The velocity, V, of sound in a gas is given by the equation

$$V = \sqrt{\frac{\gamma P}{\rho}},$$

where P = the pressure of the gas, and ρ its density.

Evidently, if any gases are to behave as though their molecules were smooth spheres, monatomic gases would be the most likely ones to do so. We have direct evidence that mercury vapour consists of monatomic molecules (see Chap. XII (B)). In 1876 Kundt and Warburg determined the velocity of sound in mercury vapour, using their well-known method, and found

$$\gamma = 1 \cdot 666$$

This is a most striking agreement. It is almost inconceivable that the molecules of mercury vapour are really smooth spheres; in fact, we know that they are not. Yet in this respect they seem to behave as though they were.

The importance of this agreement lies in the fact that, though the assumptions of the simple kinetic theory regarding the nature of gaseous molecules must be a gross simplification of the actual structure of the molecules, it would seem that some weight can be attached to the value of γ obtained with real gases. In particular, the value of 1·67 for γ leads to some important conclusions regarding the nature of the molecule. These will be considered in the next section.

More Complex Molecules.—A molecule which is not merely a hard smooth sphere can possess energy in other ways than by merely moving about. It can, for example, rotate, spinning round like a top.* When a gas consisting of such rotating molecules is heated, we must suppose not only that the molecules move about more quickly, but also that they spin more rapidly. Hence, to raise the temperature of such a gas through 1 degree, heat must be supplied not only to increase the kinetic energy of translation, but also the kinetic energy of rotation.

It is not necessary to confine ourselves to translation and rotation; vibrations within the molecule may be set up, which increase in vigour as the temperature rises.

All these modes in which a molecule can possess energy otherwise than by translation are conveniently summed up by saying that the molecule possesses "internal energy."

The general bearing which this will have upon the specific heat ratio is easily seen. The molecular heat at constant volume will be greater than with an ideal monatomic gas, because of the additional heat which goes to increase the internal energy of the molecules. Let us denote this additional quantity of heat, or of energy (the terms are interchangeable), by the symbol ϵ.

Then

$$C_v = \tfrac{3}{2}R + \epsilon \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The molecular heat at constant pressure will be given, as before, by the equation

$$C_p = C_v + R = \tfrac{5}{2}R + \epsilon.$$

Hence the ratio

$$\gamma = \frac{C_p}{C_v} = \frac{\tfrac{5}{2}R + \epsilon}{\tfrac{3}{2}R + \epsilon} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The greater the internal energy of the molecule, the smaller the value of γ. (As ϵ increases, so γ tends towards unity.) Hence we may expect that gases containing complex molecules

* A smooth sphere can, of course, rotate; but the rotation of a molecule consisting of a smooth sphere is not affected by collisions with other molecules, which is the point at issue.

will give smaller values of γ than gases consisting of relatively simple molecules ; and this is in general the case. Compare the following examples :

Gas.	Number of Atoms in Molecule.	γ.
Mercury vapour	1	1·666
Hydrogen	2	1·41
Oxygen	2	1·40
Nitrogen	2	1·41
Chlorine	2	1·36
Hydrogen chloride ..	2	1·40
Carbon monoxide ..	2	1·40
Nitric oxide	2	1·39
Mean value of γ for 7 diatomic gases =		1·40
Water vapour	3	1·305
Carbon dioxide	3	1·30
Hydrogen sulphide ..	3	1·34
Sulphur dioxide	3	1·26
Mean value of γ for 8 triatomic gases =		1·30
Methane	5	1·31
Chloroform	5	1·15
Methyl alcohol	6	1·26
Ethyl alcohol	9	1·13
Diethyl ether	15	1·02

It will be evident that there is a general relationship between the value of γ and the complexity of the molecule. Diatomic gases give values of about 1·4, triatomic about 1·3, and polyatomic gases values which tend to decrease as the number of the atoms in the molecule increases.

We may pause for a moment to consider the value for mercury vapour. It may well be asked why, even if the molecule be regarded as spherical, it should not possess energy of rotation. It is hardly possible to discuss this fully in a few words, but we may consider that the value of 1·666 for γ indicates that on raising the temperature of this vapour all the energy supplied goes to increase the energy of translation, and none to increase the internal energy, of the molecules.

GENERAL SUMMARY OF THE PRECEDING THEORY

From the three fundamental assumptions of the kinetic theory, given on p. 167, it is possible to deduce the following equation:

$$pv = \tfrac{1}{3}nmc^2,$$

where p = the pressure of the gas,
v = its volume,
n = the number of molecules present in this volume,
m = the mass of each molecule,
c = the "root mean square velocity," which to a sufficiently close approximation may be taken as the average velocity of the molecules.

Applying Boyle's Law to this equation, we deduce that the mean kinetic energy of the molecules of a gas remains constant, provided the temperature does not alter.

From Avogadro's hypothesis, it also follows that when two gases are at the same temperature and pressure, the mean kinetic energies of their molecules are equal.

Applying Charles's Law, we find that the mean kinetic energy of the molecules of a gas is directly proportional to the absolute temperature.

Conversely, if, on "general mechanical principles," we start by assuming the above statements regarding the kinetic energies of the gas molecules, we can deduce Boyle's Law, Avogadro's Hypothesis, and Charles's Law as consequences of the above equation.

The "molecular heat" of a gas is defined as the number of calories required to raise the temperature of a gram-molecule of a gas through 1 degree. If an ideal monatomic gas be kept at constant volume, all the heat supplied goes to raise the temperature of the gas, that is, to increase the kinetic energy of translation of the molecules. (Kinetic energy of translation is the energy which the molecules

possess by virtue of their motion from one place to another.) If the gas be kept at constant pressure, an additional amount of heat has to be supplied to raise its temperature 1 degree, owing to the expansion of the gas against the external pressure. It can be shown that if C_v = molecular heat at constant volume, C_p = molecular heat at constant pressure,

$$\frac{C_p}{C_v} = \gamma = 1{\cdot}67.$$

This value has been obtained for mercury vapour, which is known (see Chap. XII (B)) to be monatomic.

If a molecule, besides moving about, rotates or vibrates, it possesses energy other than kinetic energy of translation, and is said to possess *internal* energy. The molecular heat at constant volume of a gas consisting of such molecules will be greater than that of the simple gas previously considered, owing to the need for supplying heat to increase the internal energy. If ϵ be the amount of heat required to increase the internal energy of the molecules when a gram-molecule of the gas is raised in temperature by 1 degree, then

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R + \epsilon}{\frac{3}{2}R + \epsilon}.$$

Hence the larger the internal energy of the molecules, the more nearly will the value of γ tend towards unity.

It is found (see Table, p. 178) that the more complex the molecules of a gas, the smaller, in general, is the value of γ.

The value of 1·666 for mercury vapour must be taken to indicate that all the heat supplied to this vapour goes to increase the kinetic energy of translation of the molecules.

ATOMIC WEIGHTS OF THE RARE GASES

It is well known that, as a result of very accurate determinations of the densities of some elementary gases, Lord Rayleigh found that atmospheric nitrogen, prepared by removing the oxygen from air, appeared to have a density about 0·5 per cent. greater than that of nitrogen prepared by various chemical means. Two explanations of this difference were possible :

(1) Chemically prepared nitrogen might contain a lighter gas, such as hydrogen.

(2) Atmospheric nitrogen might contain a heavier gas, possibly a polyatomic form of nitrogen.

By dint of various experiments, such as passing chemically prepared nitrogen over red-hot copper oxide, and by submitting both kinds of nitrogen to the action of the electric discharge, Rayleigh satisfied himself that explanation (1) was untenable. By submitting atmospheric nitrogen to the action of heated magnesium, he showed that the second explanation was correct. The magnesium absorbed the nitrogen, leaving an inert gas of greater density. At the end of a long research, this heavier constituent of the atmosphere was isolated ; the density of the gas, from the analysis of seven samples, was found to be 19·90, a figure later altered to 19·94.

The new gas was found to be chemically quite inert, and incapable of combining with the most varied reagents. It was considered both by Rayleigh and Ramsay, who were jointly concerned in the investigation, to be most unlikely that the gas was an allotropic form of nitrogen ; and they regarded it as a new element, to which they gave the name " Argon " (idle), and the symbol A.

A discovery of the greatest importance was thus made as the result of density measurements more accurate than any previously made ; the discovery was described by

Lord Rayleigh as "the triumph of the last place of decimals."

The next problem awaiting solution was that of the atomic weight of argon. Owing to its chemical inertness, it was manifestly impossible to determine the atomic weight by the standard method of Cannizzaro. The following quotation is taken from Travers (*The Discovery of the Rare Gases*):

"It was, of course, impossible to obtain any chemical evidence as to the atomic weight of the new element, supposing the gas were really elementary. However, assuming the validity of the law of Avogadro, which even the most critical chemist would hardly have been prepared to question, the relationship between the atomic weight and the density of the gas would depend on the constitution of the molecule."

The density of the gas being 19·9, its molecular weight will be 39·8, or nearly 40. The following, therefore, represent possible values of the atomic weight of argon:

Constitution of the Molecule.	Symbol	Atomic Weight.
Monatomic	A	40
Diatomic	A_2	20
Triatomic	A_3	13-14
Tetratomic	A_4	10

"The chemical method being inapplicable to the solution of the problem, the first question which would arise would be, Did the periodic law indicate any particular value for the atomic weight?"

The result of this query was a very interesting controversy. It must be remembered that about this time (1895) the Periodic Law was not accepted so universally as it is to-day; and, as Travers goes on to point out,

"Curiously enough, a firm faith in the Periodic Law was more of a hindrance than a guide at the outset."

Reference to the Periodic Table will show the following regarding the position of argon:

	Possible Atomic Weight of Argon.	Position.
(1)	10	Between beryllium and boron.
(2)	13–14	Between carbon and nitrogen.
(3)	20	Between fluorine and sodium.
(4)	40	Between potassium and calcium.

The first of these can be ruled out as inconceivable; an atomic weight of 13–14 would likewise result in a most improbable position. Both of these would utterly derange the periodic classification.

On the other hand, it was quite possible that a group of elements might be discovered lying between the extremely electro-negative halogens and the extremely electro-positive alkali metals; and elements of this group might be expected to exhibit "neutral," or inert, characteristics.

Argument from the Periodic Table, therefore, appeared to indicate that the new element was a diatomic gas, of atomic weight 20, lying between fluorine and sodium.

In December, 1894, however, Ramsay determined the ratio of the specific heats of the gas, using Kundt and Warburg's method. The value of γ he obtained was 1·653. This was slightly below the theoretical value for a monatomic gas (1·67), but very much closer to it than to the mean value for diatomic gases (1·40).

This result, therefore, seemed to indicate that argon was monatomic. The evidence provided by the specific heats, however, was at least debatable, and it is interesting to see what Ramsay and Rayleigh themselves said of it. The former, in a paper published in 1895, wrote:

". . . If, as for mercury vapour, or for argon, the ratio of the specific heats $C_p : C_v$ be $1\frac{2}{3}$rds, it follows . . . that the whole kinetic energy of the gas is accounted for by the translatory motion of its molecules. In the case of mercury the absence of intra-atomic energy" (*i.e.* that which we have called internal energy) "is regarded as proof of the monatomic character of the vapour, and the conclusion holds equally good for argon.

"The only alternative is to suppose that if argon molecules are diatomic, the atoms acquire no relative motion, or even rotation, a conclusion improbable in itself, and one postulating the sphericity of such a complex group of atoms."

Lord Rayleigh, in a discussion held at a meeting of the Royal Society, likewise pointed out that a specific heat ratio of 1·66 implies that there is no increase, with rise of temperature, either of rotational energy of the molecule, or of movement among the atoms in the molecule. He stated it as his opinion that argon must be monatomic, adding:

"No doubt the whole subject is one about which we know exceedingly little, mercury vapour being the only gas which exhibits a similar property."

Those who believed that argon was monatomic, however, had to admit that its atomic weight was anomalous; for, if the gas were to be fitted in between a halogen and an alkali metal, its atomic weight should have been less than that of potassium, which was known to have an atomic weight of 39·1; and that of argon, if the gas were monatomic, was apparently 39·9.

Many attempts were made to see if argon were a mixture of gases: liquid argon was allowed to boil, which it did at constant temperature; some of the gas was allowed to diffuse, but no difference in density between the diffused and undiffused fractions could be detected; the gas was shaken with water, and the spectra of the dissolved and undissolved portions compared, without any noticeable difference. (Later, crude argon *was* found to contain other gases, but in very small amount.)

It was suggested that argon might contain a small proportion of diatomic molecules. Though this suggestion could not, on the evidence available, be dismissed altogether, it gained little support. Friend (*The Theory of Valency*) writes (1908):

"Until further research has been done on the subject, we must be content to regard argon as an exception to the Periodic Law."

The Other Rare Gases.—The argument in favour of the monatomicity of argon received strong confirmation by the discovery, very shortly afterwards, of the remaining gases of the group. In 1895 Ramsay succeeded in isolating, from the gas given off by the radio-active mineral clèveite (which contains uranium), the element helium. It was found to have a spectrum identical with some of the Fraunhofer lines noticed in the solar spectrum by Lockyer in 1868 (the particular line noticed by Lockyer was one in the yellow, almost coincident with the double line of sodium). The density of the gas was found to be almost exactly 2, and the ratio of the specific heats at constant pressure and constant volume 1·66.

The gas was therefore regarded as monatomic, of atomic weight 3·99 or 4·00; it forms the first member of the group, lying between hydrogen and lithium.

The rapidly improving technique of manipulating gases at low temperatures led to the isolation, by the fractional distillation of argon, of the following gases:

Helium and Neon (obtained from the gases *first* evolved on the evaporation of liquid air).

Krypton and Xenon (from the *last* portions of gas evolved on evaporating large quantities of liquid air).

The following table gives the densities, the specific heat ratios, and the atomic weights of these gases:

Gas.	Vapour Density (O = 16).	$\frac{C_p}{C_v}\left(=\gamma\right)$.	Atomic Weight.	Position in Periodic Table.
Helium ..	2·00	1·67	4·00	Between hydrogen and lithium.
Neon ..	10·1	1·64	20·2	Between fluorine and sodium.
Argon ..	19·95	1·67	39·9	Between potassium and calcium (anomalous).*
Krypton..	41·46	1·69	82·92	Between bromine and rubidium.
Xenon ..	65·1	1·67	130·2	Between iodine and cæsium.

* For the explanation of this anomaly, see Chap. XXI.

The discovery of the entire group of gases, and the fact that γ in all cases approached very nearly to the value of 1·67, finally silenced criticism, and the gases were universally accepted as being monatomic.

NOTE.—Among the radioactive elements, in the last incomplete series of the Periodic Table, the gas "Niton," or "Radon," has been isolated, as an emanation from radium. Ramsay and Gray undertook, in 1909, to determine the density of the gas, and obtained the value of 111·5 for the vapour density, which gives an atomic weight of 223.* Their work must stand as one of the most remarkable density determinations which have ever been made, since they had at their disposal only 0·1 cubic millimetre of gas. Their results were sufficient to confirm the value of 222·4 for the atomic weight of radon, a value deduced by subtracting the weight of one α-particle (a charged helium atom) from the known atomic weight of radium. For further information in this connection, an account of the radioactive elements should be consulted.

APPENDIX TO CHAPTER XV

AN EXTENSION OF THE KINETIC THEORY OF GASES TO EMBRACE POLYATOMIC MOLECULES

It has been shown above that most diatomic gases give a value for γ of almost exactly 1·40. This is in remarkable agreement with a theorem developed by Maxwell and Boltzmann, commonly known as the "Theorem of Equipartition of Energy"; and though even a brief discussion of this subject takes us into somewhat speculative regions, it may be of interest to give the matter of it in bare outline.

Consider an ideal monatomic gas. We have seen that the velocity of any single molecule of the gas may be resolved along three axes, each at right angles to one another; if the

* The gas lies in Group O of the Periodic Table.

velocity be c, and x y and z the components of the velocity along the three axes, then

$$c^2 = x^2 + y^2 + z^2 \quad . \quad . \quad . \quad . \quad (13)$$

The kinetic energy of the molecule is $\frac{1}{2}mc^2$. Hence

$$\tfrac{1}{2}mc^2 = \tfrac{1}{2}mx^2 + \tfrac{1}{2}my^2 + \tfrac{1}{2}mz^2 \quad . \quad . \quad (14)$$

This kinetic energy has thus been divided into three components. If the velocity of the molecule *parallel to one axis* were by some means increased, the components of the velocity parallel to the other two axes would remain unchanged, since the axes are mutually rectangular. There are thus three possible directions in which the velocity might alter, these directions being in a sense independent of one another. The same applies to the kinetic energy of translation of the molecules.

In such a case, we say that the molecule has three *degrees of freedom*.

This is a somewhat crude attempt to give a physical picture of what is meant by a degree of freedom; we may alternatively describe the number of degrees of freedom of a system as the number of independent co-ordinates by means of which the energy may be completely expressed. In this case we have three such co-ordinates, namely, the three rectangular axes.

If we consider a gas confined in the cube given in Fig. 3 (p. 169), we know by experience that the pressure exerted by the gas is uniform on all the walls of the cube; we do not find that it is greater, for example, on two opposite faces than on the remaining four. Considerations of this kind led to the enunciation of the theorem of equipartition of energy, which states that

In a system in equilibrium, the energy is equally divided among all the degrees of freedom.

Actually, in the cube, the molecules will be moving in all possible directions. If $\frac{1}{2}mc^2$ represents the kinetic energy of a single molecule, the total kinetic energy of all the molecules may be represented by the symbol $\Sigma\frac{1}{2}mc^2$. Hence, from equations (13) and (14),

$$\Sigma\tfrac{1}{2}mc^2 = \Sigma\tfrac{1}{2}mx^2 + \Sigma\tfrac{1}{2}my^2 + \Sigma\tfrac{1}{2}mz^2 \quad . \quad . \quad (15)$$

The theorem of equipartition of energy states that in equilibrium

$$\Sigma\tfrac{1}{2}mx^2 = \Sigma\tfrac{1}{2}my^2 = \Sigma\tfrac{1}{2}mz^2 \quad . \quad . \quad . \ (16)$$

Now, in an ideal monatomic gas, equation (7) states that the total kinetic energy, E, of the molecules in a gram-molecule of the gas is equal to $\frac{3}{2}$RT. Since this energy is equally divided among the three degrees of freedom, we reach the important result that

In a gram-molecule of a gas in equilibrium, the energy possessed by each degree of freedom is equal to $\frac{1}{2}$RT.

An Ideal Diatomic Gas.—We can picture the molecule of an ideal monatomic gas as a hard smooth sphere. Imagine now two such spheres joined together (Fig. 4).

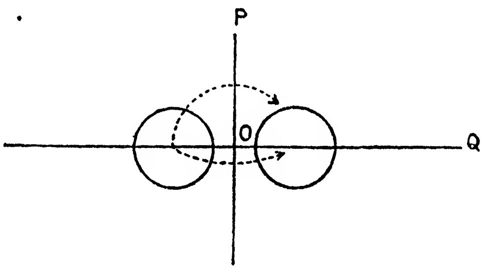

FIG. 4.

In addition to moving about as a whole, such a molecule could rotate; and just as we can resolve its translational motion along three rectangular axes, so we can resolve its rotational motion about two axes at right angles to one another; these axes are OP, and a line passing through O at right angles to the plane of the diagram. (We disregard rotation about OQ, just as we disregard possible rotation of the spherical monatomic molecule.)

Hence, in addition to possessing three degrees of freedom of rotation, this ideal diatomic molecule will possess two degrees of freedom of rotation (it is possible, for example, to imagine the speed of rotation about OP to be increased,

without affecting the rotation about the second axis). We obtain the result that

In a gram-molecule of an ideal diatomic gas, the total kinetic energy of the molecules is equal to $\frac{5}{2}$RT;

since the system has 5 degrees of freedom, 3 of translation and 2 of rotation, and each possesses kinetic energy equal to $\frac{1}{2}$RT.

It follows, on the same lines as those adopted in deducing equation (8), that the molecular heat at constant volume of such a gas is given by

$$C_v = \tfrac{5}{2}R;$$

and, by equation (9),

$$C_p = \tfrac{7}{2}R.$$

Hence,

$$\frac{C_p}{C_v} = \gamma = \tfrac{7}{5} = 1{\cdot}40.$$

The agreement between this figure and the value of γ actually obtained for a number of diatomic gases (see Table, p. 178) is certainly striking. Nevertheless, there are several reasons why the results should be accepted only with caution. These are too numerous and too involved to be given here at length, but one or two may be mentioned, in case the student should imagine that the career of the simple kinetic theory were an unbroken series of triumphs.

In the first place, it will be observed from the Table that γ for chlorine is much lower than the "predicted" value of 1·40, and that it lies nearer to the value which may be calculated for a gas whose molecules possess 6 degrees of freedom.* If we knew nothing else about the structure of the chlorine molecule, we might have been tempted to conclude that it was triatomic, possessing a molecule capable of rotation about *three* rectangular axes.

Again, we have seen that the molecular heat at constant

* It is easily seen that for a gas whose molecules possess n degrees of freedom, the ratio C_p/C_v is given by $\frac{n+2}{n}$; if $n = 6$, $C_p/C_v \doteq 1{\cdot}33$.

volume of an ideal diatomic gas should have the value $\frac{5}{2}R$. Measured in calories per degree, this equals

$$\tfrac{5}{2} \times 1{\cdot}9885 = 4{\cdot}97 \text{ cal./deg.}$$

Actual values obtained for diatomic gases include the following :

Hydrogen	4·87 cal./deg.
Oxygen	5·04 ,,
Nitrogen	4·93 ,,
Chlorine	5·93 ,,
Nitric oxide	4·95 ,,

The deviations shown by several of these gases lie well outside experimental error ; the simple kinetic theory, based on the principle of equipartition of energy, is unable to account for these deviations.

Another phenomenon for which this theory cannot account is that known as the "Degradation of Gases." It may be illustrated by the example of hydrogen. The specific heat of hydrogen falls as the temperature is lowered, reaching at very low temperatures the value of 3 calories, which is the theoretical value for an ideal monatomic gas ($\frac{3}{2}R$ — equation (8)). It is as though at low temperatures the hydrogen molecule lost some of its degrees of freedom. This would appear quite incomprehensible on the "Classical" Theory (*i.e.* the theory based on classical mechanics which we have been considering).

These few considerations will show that the theorem of equipartition of energy, applied to the results of the kinetic theory, does not suffice to explain all the phenomena exhibited by gases. We are not justified in taking only those results which support facts already discovered independently, and in ignoring the others. One is entitled, perhaps, to consider that the value of 1·40 for γ in the case of hydrogen and some other gases affords *corroborative evidence* of their diatomicity ; but this evidence should not for a moment be considered as equal in weight to that supplied by Cannizzaro. In this connection it is worth noting that many physicists, at the end of the nineteenth century, held all this reasoning to be "absolutely unsound" (Travers, *loc. cit.*) ; and though some explanation of such phenomena as the degradation of gases has

been advanced recently on the basis of the quantum theory, the elementary student is advised to keep out of such deep waters.

GENERAL SUMMARY OF THE APPLICATION OF THE KINETIC THEORY TO THE DETERMINATION OF THE ATOMICITY OF GASES

We have seen (pp. 175, 176) that the kinetic theory leads to the result that the ratio

$$\frac{\text{Molecular heat at constant pressure}}{\text{Molecular heat at constant volume}}$$

should be equal to $\frac{5}{3}$, or 1·67 for an "ideal monatomic gas," that is, when all the heat supplied in raising the temperature of the gas goes to increase the kinetic energy of translation of the molecules, and none towards increasing their internal energy.

In the case of mercury vapour, we have chemical evidence that the molecules consist of single atoms of mercury. In the case of the rare gases, if we calculate their atomic weights from their vapour densities, on the assumption that the gases are monatomic, we obtain values which place all the gases in a single group of the Periodic Table just where the existence of such a group is most probable. (The atomic weight of argon is "anomalous," but the anomaly has now been explained.)

Mercury vapour, and the rare gases, all give ratios of C_p/C_v which lie very close to the value 1·67. This may be accepted (1) as confirming their monatomicity, and/or (2) indicating that monatomic gas molecules behave very much like the "ideal" molecule of the kinetic theory.

If molecules possess internal energy, the ratio C_p/C_v is less than 1·67; the greater the relative amount of internal energy of the molecule compared with its trans-

lational energy, the more nearly does the ratio approach unity. (See pp. 177, 178.)

The ideal diatomic molecule, according to the kinetic theory, consists of two atoms rigidly held together (Fig. 4, p. 188). Such a molecule could not only move about as a whole; it could also rotate. Hence, besides possessing kinetic energy of translation, it will possess internal energy, due to its rotation. For a gas consisting of such molecules, the ratio C_p/C_v should be less than 1·67; and it is possible, from certain theoretical considerations based on the principle of "equipartition of energy," to calculate that the ratio should be 1·40. Certain gases known to be diatomic give a ratio very near to this figure; they include hydrogen, oxygen, and nitrogen. Chlorine, however, gives a lower value.

This figure of 1·4 actually obtained with certain gases may be taken as *confirmatory* evidence that the gases in question are diatomic. The reasoning is somewhat abstract, however, and all the predictions which should follow from it are not in practice fulfilled.

In conclusion, it may be repeated that a ratio of 1·67 for C_p/C_v may be taken as direct evidence that all the heat supplied to the gas in question goes to increase the kinetic energy of translation of the molecules, and therefore that there is a strong indication that the gas is monatomic. If a ratio of 1·4 be found, the probability is that the gas is diatomic; but it would be unwise to place much reliance upon the result in the absence of confirmatory evidence from other sources.

References

The simple kinetic theory, and its extension by van der Waals, is described in most text-books of Physical Chemistry, *e.g.*:

Introduction to Physical Chemistry, by James Walker. (Macmillan, 16*s*.)

A Class-Book of Physical Chemistry, by Lowry and Sugden. (Macmillan, 6*s*. 6*d*.)

A fuller account, including the distribution of velocities of the molecules, is given in larger works such as Preston's *Theory of Heat*. (Macmillan, 25*s*.)

A non-mathematical account of the theorem of equipartition of energy (not dealing, however, with " degrees of freedom "), including its fascinating application to the problem of the age of the universe, will be found in *The Universe Around Us*, by Sir James Jeans. (Camb. Univ. Press, 12*s*. 6*d*.)

The Rare Gases.

Original papers by Ramsay and Rayleigh include the following:

Phil. Trans., **186**, A, 187 (1895).
Journ. Chem. Soc., **67**, 1107 (1895).
British Assoc. Rep., 595 (1897) ; 828 (1898).
Proc. Roy. Soc., **63**, 405 (1898).

A general account may be found in Ramsay's *The Gases of the Atmosphere* and in *The Discovery of the Rare Gases*, by Travers (Arnold, 15*s*.). In the latter book much interesting personal material is collected, including reproductions from note-books used by the investigators.

The account of the determination of the density of " Niton " is given in *Proc. Roy. Soc.*, **84**, A, 536 (1911).

Exercises on Chapter XV

1. From equations (1) and (2), pp. 164–5, deduce the relationship between the temperature and pressure of a gas when its volume is kept constant.

2. Assuming the truth of the following statements:

(*a*) At constant temperature the average kinetic energy of the molecules of an ideal gas remains constant ;

(*b*) When two gases are at the same temperature and pressure, the average kinetic energies of their molecules are equal ;

deduce from equation (4), p. 171, Boyle's Law and Avogadro's Hypothesis.

3. What is the relationship between the mean velocity of a gas molecule and the absolute temperature ?

4. Write a short account (about 400 words) describing how the atomic weights of the rare gases were determined.

5. The specific heats of an elementary gas (in calories per gram per degree C.) are found to be 0·74 and 0·123, measured at constant volume and constant pressure respectively.

150 c.c. of the gas, at 15° C. and 745 mm. pressure, weigh 0·2484 grm.

What conclusion can you draw regarding the probable atomic weight of the element?

6. The specific heats of an elementary gas are found to be 0·175 and 0·235, at constant volume and constant pressure respectively. What conclusion can you draw regarding the molecules of the gas?

CHAPTER XVI

GENERAL SUMMARY OF ATOMIC WEIGHT DETERMINATIONS

In this chapter the general principle underlying accurate atomic weight determinations will be restated, together with references to the methods which have been employed in determining the atomic weights of various classes of elements.

Atomic Weight and Equivalent Weight.—*Hydrogen Standard.*)—On this standard, the equivalent weight of an element is defined as that weight of the element which will combine with, or displace, unit weight of hydrogen; and the atomic weight as the weight of the atom of the element compared with the weight of an atom of hydrogen. It may readily be shown that the atomic weight is simply connected with the equivalent weight.

Consider an element, X. According to Dalton's theory, 1 atom of X will combine with, or displace, nX atoms of hydrogen, where n is a *small whole number* (see p. 74, *d*). (It is conceivable that n might be a rational fraction; for example, it might require 2 atoms of X to displace 1 atom of hydrogen. In practice, however, it is found that n is never less than 1.)

Taking the gram as our unit of weight, we obtain the following:

$$1 \text{ atom of X} \left\{ \begin{matrix} \text{combines with} \\ \text{or displaces} \end{matrix} \right\} n \text{ atoms of hydrogen.}$$

$$\begin{matrix} 1 \text{ atomic weight of X} \\ \text{(in grams)} \end{matrix} \left\{ \begin{matrix} \text{combines with} \\ \text{or displaces} \end{matrix} \right\} n \text{ grams of hydrogen}$$

(the atomic weight of hydrogen being, by definition, equal to 1).

Hence 1 gram of hydrogen is equivalent to

$$\frac{\text{the atomic weight of X (in grams)}}{n} = \left\{\begin{array}{l}\text{the gram-}\\\text{equivalent}\\\text{weight of X.}\end{array}\right.$$

In general terms,

$$\text{the equivalent weight of an element} = \frac{\text{the atomic weight}}{n}$$

or

$$\text{the atomic weight of an element} = \text{the equiv. wt.} \times n,$$

where n is a small whole number, which may be called the valency of the element.

In practice, determination of the atomic weight of an element almost invariably consists of two independent experiments :

(1) The accurate determination of the equivalent weight of the element ;

(2) Determination of the atomic weight with sufficient accuracy to enable n to be found.

The accurately determined equivalent is then multiplied by n, giving the accurate atomic weight.

(1) **Determining Equivalent Weights.**—It is not necessary to restrict experiment to analysis or synthesis of hydrides, or to direct displacement of hydrogen. The Law of Equivalents (see Chap. VII) states that *weights of two elements which are equivalent to the same weight of a third element are equivalent to one another.* Hence, if we find, for example, the weight of oxygen which combines with unit weight of hydrogen, the equivalent weight of a third element may be found by determining the weight of it which combines with this weight of oxygen.

It is important to realise that the determination of equivalent weights is independent of any theory as to the structure of matter ; it consists simply in the experimental measurement of the relative weights in which elements combine with one another.

The Oxygen Standard.—Many elements will not combine with or displace hydrogen, but nearly all will combine with oxygen. For this reason, many chemists in the nineteenth century preferred to make oxygen, rather than hydrogen, the standard element; and this choice was found to have certain further advantages (see next chapter). The "hydrogen standard" is now everywhere abandoned, and the present definition of equivalent weight is as follows:

> *The equivalent weight of an element is that weight of it which will combine with* **exactly** 8 *units by weight of oxygen, or with the equivalent weight of any other element.* (This includes also the possibility of displacement of one element by another, in equivalent proportions.)

Experimental Determination of Equivalents.—A complete account of the various methods used is beyond the scope of this book; some of the principal ones will be mentioned. For a further description, a text-book of Inorganic Chemistry should be consulted.

(*a*) **Formation of Oxide.**—This is a method of general application in determining the equivalent weights of many metals. A weighed quantity of the metal may be treated with concentrated nitric acid, and the product evaporated to dryness and heated until fumes cease to be evolved. It is then cooled and weighed; more nitric acid is added, and the process repeated until constant weight is obtained.

Among the metals suitable for this treatment are copper, bismuth, and tin.

In certain cases, the oxide may be formed in a slightly different way; thus, in finding the equivalent weight of ferric iron, a weighed quantity of iron may be dissolved in dilute sulphuric acid (giving a solution of ferrous sulphate), the ferrous solution oxidised by boiling with excess of nitric acid, the iron precipitated as ferric hydroxide by adding excess of ammonia, and the precipitate ignited and weighed as ferric oxide.

An example of particular importance is the gravimetric composition of water. Dumas' experiment consisted in passing carefully purified hydrogen over a weighed quantity of heated copper oxide. The water formed was collected and weighed ; the loss in weight of the copper oxide gave the weight of oxygen present in this weight of water.

The combining ratio has since been determined with greater accuracy by Morley and others (see next chapter).

(*b*) **Reduction of Oxide.**—Certain metallic oxides may be readily reduced by heating to redness in a stream of hydrogen or carbon monoxide. The reducing gas must, of course, be carefully purified from any substance, such as sulphuretted hydrogen, which might combine with the metal.

(*c*) **Displacement of Hydrogen.**—This method, though familiar to most candidates for the School Certificate and similar examinations, is not much used for accurate work. It consists in dissolving a weighed quantity of the element in excess of acid (in some cases, caustic alkali can be used), and measuring the volume of hydrogen evolved. The weight of the hydrogen can be found by correcting to N.T.P., and using the value for the density of hydrogen under these conditions.

(*d*) **Analysis of Hydrides.**—Few hydrides are suitable for exact analysis. The equivalent weight of chlorine has, however, been determined with great accuracy from the " limiting density " of hydrogen chloride (see next chapter). This equivalent weight is of the greatest importance, as will be seen in the next paragraph.

(*e*) **Analysis (and Synthesis) of Chlorides.**—This is one of the methods most widely used. Knowing the equivalent weight of chlorine, it is possible to find the equivalent weight of silver by dissolving a known weight of pure silver in dilute nitric acid, and precipitating the silver as chloride. Some extremely accurate experiments have been performed on these lines, in which the minute amount of silver chloride which goes into solution has been carefully estimated.

From this starting point, the equivalent weights of many other elements may be found, by preparing the pure chloride, dissolving a given weight in dilute nitric acid, and precipitating all the chlorine by adding excess of silver nitrate solution. From the weight of silver chloride produced, the weight of

chlorine in the original chloride may be estimated, and hence the weight of the element in question which combines with an equivalent weight of chlorine.

Among the metals to which this method may be applied may be mentioned the metals of the alkalis and alkaline earths.

(*f*) **Analysis and Synthesis of Bromides and Iodides.**—Knowing the equivalent weight of silver, those of bromine and iodine may be found by converting a known weight of pure silver into the bromide or iodide.

Bromides and iodides may also be used in place of chlorides, by proceeding along the same lines as in method (*e*).

(*g*) **Method of Replacement.**—Certain metals will displace others from solutions of their salts (*e.g.* zinc or iron will displace copper from a solution of copper sulphate). When this occurs, replacement takes place in equivalent proportions. If the equivalent weight of one of the two metals is known, that of the other can readily be calculated.

(*h*) **By Electrolysis.**—Faraday's Second Law of Electrolysis states that elements are liberated in the ratio of their chemical equivalents. For example, the passage of an electric current which liberates 1 gram-equivalent of hydrogen from dilute sulphuric acid will also cause the deposition of 1 gram-equivalent of copper from a solution of copper sulphate.

In addition to these methods, others less direct have been often employed. As one example, we will consider the determination of the equivalent weight of nitrogen by the conversion of a weighed amount of potassium chloride into potassium nitrate. The equivalent weights of potassium, chlorine, and oxygen being known (methods (*e*), (*d*), and (*a*) respectively), that of nitrogen can be calculated from the weight of potassium nitrate which is formed.

Further details of methods, and of their application to particular elements, will be found in Ostwald's *Outlines of General Chemistry* (Macmillan). Descriptions of more recent work may conveniently be found in the Annual Reports of the Chemical Society.

(2) **Experimental Determination of Atomic Weight.**—The principal means employed are (*a*) the vapour density method of Cannizzaro; (*b*) Dulong and Petit's Law; (*c*) the Law of Isomorphism; (*d*) the position of the element in the Periodic Table; (*e*) (for certain gaseous elements) the ratio of the specific heats at constant pressure and constant volume, combined with the vapour density of the element.

(*a*) The vapour densities of as many compounds of the element as may be vaporised without decomposition are found, and the weights of the element present in a molecular weight of the various compounds calculated from this and from the percentage composition of the compound.

The weight of the element present in a molecular weight of any compound will be nW, were W is the atomic weight, and n represents the number of atoms of the element present in the molecule. Hence the various values of nW which are found by this method will always be divisible by a constant factor; and unless all the compounds chosen contain an even number of atoms of the element in their molecules, this factor will be equal to W.

Since n cannot be *less* than 1, the product nW cannot be less than the atomic weight of the element. Hence the application of this method to a single compound will give the maximum atomic weight which the element can possess.

(For further details, see Chap. XI.)

(*b*) The specific heats of the majority of *solid* elements, multiplied by their respective atomic weights, give values which are approximately constant. The numerical value of the constant was shown by Cannizzaro to be about 6·4; Cannizzaro considered for this purpose the specific heats of solid bromine, iodine, and mercury, as the probable atomic weights of these elements were already known by method (*a*).

The above product is known as the *atomic heat*. Dulong and Petit's law may therefore be stated as follows :

The atomic heats of most solid elements are approximately equal to 6·4.

Kopp's law states that the molecular heat of a compound (*i.e.* the product of the molecular weight and the specific heat) is equal to the sum of the atomic heats of the element composing the molecule. By means of this law, the atomic heats of certain elements can be found or confirmed.

(See Chaps. XII (A) and XII (B).)

(*c*) Compounds which are isomorphous have similar molecular structures. Hence, if the molecular structure of one of two isomorphous compounds is known, that of the other is also known ; and, from the percentage composition of the latter, the atomic weight of a particular element contained in it can be deduced.

(See Chaps. XII (A) and XIV: also Exercises on pp. 203, 204.)

(*d*) The physical and chemical properties of the elements are periodic functions of their atomic weights Hence, in general, a given element must be assigned a certain approximate atomic weight in order that it may be fitted into the periodic classification. (Chap. XIII.)

(*e*) *Ratio of Specific Heats.*—The kinetic theory of gases leads to the conclusion that for an ideal monatomic gas the ratio

$$\frac{\text{Specific heat at constant pressure}}{\text{Specific heat at constant volume}} \text{ should equal } 1{\cdot}67.$$

Certain gases (mercury vapour, and the rare gases of the atmosphere) give this value, which indicates that they are monatomic. If this is so, their molecular weights must be equal to their atomic weights. (See Chap. XV.)

Methods (*b*)—(*d*) must be regarded as secondary methods of atomic weight determination. Though

exceedingly valuable, they rest in the first place upon the fundamental method (*a*).

The reasoning involved in method (*e*), though highly theoretical, has been confirmed by the requirements of the periodic classification. (See Chap. XV.)

Atomic Weights of the Common Elements.—In the following general survey, the following abbreviations are employed to denote the principal method or methods which have been used to fix the atomic weight :

V.D. = vapour density method of Cannizzaro.
D.P. = Dulong and Petit's law.
K = Kopp's law.
Iso = Law of Isomorphism.
S = ratio of specific heats at constant pressure and constant volume.

The periodic table may be taken as confirming generally all the values chosen ; in cases where it has been of especial importance in deciding doubtful atomic weights, the symbol **P.T.** has been inserted.

Halogens : **V.D.** ; Br. I, **V.D.** + **D.P.**

Sulphur : **V.D.**, **D.P.**

Se, Te : **V.D.** hydrides ; **Iso.** with **S** compounds.

Phosphorus : **V.D.**, **D.P.**

As, Sb, Bi : **V.D.** of chlorides ; **D.P.** ; **Iso.** with P compounds.

Carbon, Silicon, Boron : **V.D.** of hydrides, chlorides, and other derivatives : **D.P.** at high temps. (Chap. XIV.)

Beryllium : **V.D.** of chloride ; **P.T.** ; **D.P.** at high temps. (Chap. XIV.)

Metals Generally : **D.P.** (and **K**).

The **V.D.** of many chlorides can be found ; *e.g.* of Sn, Pb, etc.

Isomorphism in groups of metals is also a valuable check : *e.g.* **Iso.** of compounds of Rb, Cs, with K com-

pounds; of compounds of Sr, Ba, with certain Ca and Pb compounds; of compounds of divalent transition metals with one another, and of trivalent transition metals with one another.

Rare Gases: **S**; **P.T.**

Exercises on Chapter XVI

(*In calculating equivalent weights, the definition given on p.* 197 *should be adopted.*)

1. What is the atomic weight of the metal in question (6), Chap. VIII, if its specific heat is 0·55?

2. In a research upon the compounds of chromium, the following results were obtained:

(*a*) Chromic oxide contains 68·42 per cent. of chromium.

(*b*) Chromic anhydride contains from 50–53 per cent. of chromium.

(*c*) Potassium chromate is isomorphous with potassium sulphate.

From these results, and knowing that the molecular formula of sulphuric anhydride is SO_3 (see p. 275), derive the following:

(i) The empirical formulæ of chromic oxide and chromic anhydride.

(ii) The exact equivalent weight of chromium.

(iii) The accurate atomic weight of chromium.

Show that your conclusion regarding the atomic weight is supported by the fact that the specific heat of chromium is 0·11.

3. 0·3524 grm. of iron was dissolved in dilute sulphuric acid; the solution was oxidised by boiling with nitric acid, the iron precipitated as ferric hydroxide, and the precipitate ignited and weighed as ferric oxide. 0·5039 grm. of oxide was obtained.

Calculate the equivalent weight of iron.

Given that ferric salts are isomorphous with chromic salts

(derived from chromic oxide), calculate the atomic weight of iron.

Show that your value is confirmed by the fact that the specific heat of iron is 0·109.

3A. 0·62 grm. of iron, dissolved in dilute sulphuric acid, liberated 268 c.c. of hydrogen, collected over water at 15° C. and 757 mm. (Vapour pressure of water at 15° C. = 13 mm.)

Show how this result may be used to find the valency of iron in ferrous compounds, given the atomic weight found in (3). (1 grm. equivalent of hydrogen occupies 11·2 litres at N.T.P.)

4. 0·4325 grm. of black copper oxide was reduced in a current of hydrogen, leaving 0·3456 grm. of copper.

Given that cupric salts are isomorphous with ferrous salts, calculate the atomic weight of copper.

Show that your result is confirmed by the fact that the specific heat of copper is 0·094.

5. Potassium sulphate and selenate are isomorphous. Mitscherlich found the percentage composition of the two compounds to be

Potassium sulphate: K = 44·83, O = 36·78, S = 18·39;
Potassium selenate: K = 35·29, O = 28·96, Se = 35·75.

Given that the atomic weight of sulphur is 32·0, find that of selenium.

6. Gallium ammonium alum is isomorphous with the alum $(NH_4)_2SO_4,Al_2(SO_4)_3,24H_2O$. Both, on ignition, leave a residue of the oxide of gallium and aluminium respectively.

Lecoq de Boisbaudran, the discoverer of gallium, found that 3·1044 grms. of gallium ammonium alum left 0·5885 grm. of gallium oxide on ignition.

Calculate the atomic weight of gallium to 3 significant figures. (N = 14·01, S = 32·06, H = 1·008, O = 16·00.)

7. Rubidium alum is isomorphous with potassium alum, $K_2SO_4,Al_2(SO_4)_3,24H_2O$. Given that rubidium alum contains 5·203 per cent. of aluminium, find the atomic weight of rubidium to 3 significant figures. (S = 32·06, Al = 27·1, H = 1·008, O = 16·00.)

How could this percentage be determined experimentally?

8. 0·5484 grm. of copper was found to be displaced from a solution of copper sulphate by 0·5640 grm. of zinc.

Given (*a*) that the equivalent weight of copper = 31·8,
(*b*) that the specific heat of zinc = 0·094,
find the atomic weight of zinc.

9. In a circuit containing a copper and a silver voltameter in series, the weights of copper and of silver deposited in a given time were found to be 0·3156 grm. and 1·0705 grm. respectively.

Given (*a*) that the equivalent weight of copper = 31·8,
(*b*) that the specific heat of silver = 0·056,
find the atomic weight of silver.

PART V

THE DETERMINATION OF MOLECULAR FORMULÆ

INTRODUCTION

Finding Molecular Formulæ from Percentage Compositions and Molecular Weights

THE percentage composition of a compound (that is, the weights of the various elements present in 100 parts by weight of the compound) can be found by analytical means which vary with the nature of the compound under examination. The student will no doubt be familiar with a number of such means; and no attempt will be made to give an account of them here.

Having found the percentage composition, which gives the proportion *by weight* in which the elements are present, we can divide each percentage by weight by the atomic weight of the corresponding element. The result will be the proportions *by atoms* in which the elements are present. Since atoms cannot be divided, we must reduce the figures so obtained to whole numbers. The smallest whole numbers which stand in the correct proportion to one another will give us the simplest possible formula of the compound, which is known as the empirical formula. An example will make this clear.

A compound contains 40·00 per cent. carbon,
6·67 per cent. hydrogen,
53·33 per cent. oxygen.

What is its empirical formula?

Dividing by atomic weights, we obtain

$$\frac{40\cdot00}{12} = 3\cdot33 = 3\cdot33 \times 1$$

$$\frac{6\cdot67}{1} = 6\cdot67 = 3\cdot33 \times 2$$

$$\frac{53\cdot33}{16} = 3\cdot33 = 3\cdot33 \times 1$$

Hence the empirical formula is CH_2O.

Not all examples are as simple as this ; but it is always possible, provided the experimental data are reasonably accurate, to find a factor (in this case 3·33) which will reduce the atomic proportions to small whole numbers. (Exceptions may, of course, arise among organic and other compounds of very complex formulæ.)

The molecular formula (*i.e.* the formula expressing the actual numbers of atoms present in the molecule of the compound) may or may not be identical with the empirical formula. In the above example, it is evident that the formulæ $C_2H_4O_2$, $C_3H_6O_3$ . . . or, in general, $C_nH_{2n}O_n$, where n is any whole number, will equally satisfy the condition that the numbers of atoms of carbon, hydrogen, and oxygen present are in the ratio 1 : 2 : 1 respectively. To find the value of n, it is necessary to determine the molecular weight of the compound. The molecular weight must be a multiple by a whole number (*i.e.* a multiple by n) of the empirical formula weight.

For example, suppose that the molecular weight of the above compound were found to be 180. Then

The empirical formula weight $= 12 + 2 + 16 = 30$.

$\frac{180}{30} = 6$; hence the molecular formula is $C_6H_{12}O_6$.

This procedure brings out a point of great importance. There are a number of ways of determining molecular weights, most of which will be outlined in the following chapters. Several of them are not capable of the highest

degree of accuracy; it is usually more easy to find the percentage composition of a compound with accuracy than to find its molecular weight. But, since the percentage composition of the compound gives us its empirical formula, a very exact determination of the molecular weight is not necessary; for, if W be the empirical formula weight, and M the molecular weight of the compound, we have

$$M = nW,$$

where n is a whole number usually small; and

$$n = \frac{M}{W}.$$

Hence, any method which gives M with sufficient accuracy to enable us to determine n is adequate; and in general, a possible error of a few per cent. in the measurement of M is immaterial.

For example, in the case previously considered, it would be sufficient if we knew that the molecular weight of the compound lay, say between 175 and 185; possible molecular weights of the compound in the neighbourhood of these figures would be 150, 180, and 210, and of these 180 is evidently the correct one.

In the following chapters, the principal methods of molecular weight determination will be given in outline. While the theory of the methods will be explained, full experimental details cannot be given; they are best learnt by first-hand experience of the apparatus involved.

CHAPTER XVII

MOLECULAR WEIGHTS FROM VAPOUR DENSITIES

THE first, and perhaps most important, method of molecular weight determination consists in ascertaining the vapour density of the substance, whether elementary or compound; and the underlying theory has already been explained (Chap. XI). If we define vapour density as follows:

$$\text{Vapour Density} = \frac{\text{weight of a given volume of gas or vapour}}{\text{weight of the same volume of hydrogen}},$$

both being measured at the same temperature and pressure, then we have, by Avogadro's hypothesis,

$$\text{Vapour Density} = \frac{\text{weight of a molecule of gas or vapour}}{\text{weight of a molecule of hydrogen}}.$$

But molecular weight is defined as the ratio

$$\frac{\text{Weight of a molecule of element of compound}}{\text{Weight of an ATOM of hydrogen}}.$$

Since the molecule of hydrogen contains 2 atoms (see p. 123), then

$$\text{Molecular weight} = \text{twice vapour density.}$$

The Hydrogen and Oxygen Standards.—The above reasoning, and that contained in the previous chapters, has been based upon the "Hydrogen Standard"; that is, the atomic weight of hydrogen has been made equal

to 1, *by definition*, and other atomic weights calculated accordingly. Actually, however, this standard is now universally abandoned, and a second scale of atomic weights is used, in which the atomic weight of oxygen is, *by definition*, made equal to 16. The differences involved may be seen by the following figures :

	Hydrogen Standard.	Oxygen Standard.
Atomic Weight of Hydrogen ..	1·000	1·008
Atomic Weight of Oxygen ..	15·87	16·000
Equivalent Weight of Oxygen ..	7·94	8·000

This change of standards need not cause any confusion. The reasoning of Cannizzaro is, of course, unaffected. The student can continue to use it, adding perhaps, at the end of the theoretical argument, that at the present time all atomic and equivalent weights have been altered slightly by making the atomic weight of oxygen exactly 16. The principal reasons for this change are :

(1) Many more equivalent weights have been determined by the analysis of oxides (or synthesis of oxides) than by displacement of hydrogen. An accurate knowledge of the atomic weight of an element is always based upon an accurate determination of the equivalent (see p. 196). Using the hydrogen standard, the value obtained for the equivalent weight of an element from the analysis of its oxide depends upon an accurate knowledge of the combining ratio hydrogen : oxygen. Using the oxygen standard, equivalent weights so determined are independent of this ratio.

(2) Though the former reason was important during the nineteenth century, it is possible that a return to the hydrogen standard might have been made after the extremely accurate work of Morley (ratio of combining weights of hydrogen and oxygen = 1 : 7·9395 or 1 : 7·9396) were it not that the oxygen standard was

found to have an additional advantage. If we make the atomic weight of oxygen exactly 16, the atomic weights of very many elements approach much more nearly to whole numbers than on the oxygen scale. A few examples are given below :

	Atomic Weight. (H = 1.)	Atomic Weight. (O = 16.)
Carbon ..	11·91	12·00
Nitrogen ..	13·987	14·008
Phosphorus ..	30·79	31·04
Sulphur ..	31·81	32·06
Sodium ..	22·82	23·00
Calcium ..	39·75	40·07

Consequently, by using the oxygen standard, we are justified in taking the atomic weights of most elements to the nearest whole number, except for work of a very high order of accuracy; and the atomic weight of hydrogen (1·008) may still be taken as unity for most purposes. (An outstanding exception to the above rules is the atomic weight of chlorine, which is 35·18 on the hydrogen scale, and 35·46 on the oxygen scale.)

(Further justification for the oxygen standard is that on this scale the atomic weights of isotopes (see Chap. XXI) diverge from whole numbers by less than 0·1 per cent. except in very few cases.)

To make perfectly clear what is involved in the change from the hydrogen to the oxygen standard, parallel definitions are given below.

Equivalent Weight.

Hydrogen Standard.—The equivalent weight of an element is that weight of it which will combine with or replace unit weight of hydrogen, or the equivalent weight of any other element.

Oxygen Standard.—The equivalent weight of an element is that weight of it which will combine with or replace eight units by weight of oxygen, or the equivalent weight of any other element.

Atomic Weight.

Hydrogen Standard.—Equal to the ratio

$$\frac{\text{Weight of an atom of the element}}{\text{Weight of an atom of hydrogen}}.$$

Oxygen Standard.—Equal to the ratio

$$\frac{\text{Weight of an atom of the element}}{\text{Weight of 1/16 of the atom of oxygen}}.$$

Molecular Weight.

Hydrogen Standard.—Equal to the ratio

$$\frac{\text{Weight of a molecule of element or compound}}{\text{Weight of an atom of hydrogen}}.$$

Oxygen Standard.—Equal to the ratio

$$\frac{\text{Weight of a molecule of element or compound}}{\text{Weight of 1/16 of the atom of oxygen}}.$$

In other words, the unit of weight in measuring atomic and molecular weights, previously the weight of a hydrogen atom, is replaced by 1/16 of the weight of an oxygen atom.

Vapour Density.

Hydrogen Standard.—Equal to the ratio

$$\frac{\text{Weight of a given volume of gas or vapour}}{\text{Weight of the same volume of hydrogen}},$$

both being measured at the same temperature and pressure.

Oxygen Standard.—Equal to the ratio

$$\frac{\text{Weight of a given volume of gas or vapour}}{\text{1/16 of the weight of an equal volume of oxygen}},$$

both being measured at the same temperature and pressure.

In other words, on the hydrogen scale the density of hydrogen gas is made equal to unity; on the oxygen scale the density of oxygen is made equal to 16. In both cases,

$$\text{Molecular weight} = \text{twice vapour density}.$$

The Gram-molecular Volume.—It has been shown above (p. 165) that gram-molecular weights of *all* gases and vapours must occupy the same volume under given conditions of temperature and pressure. *The volume occupied by a gram-molecular weight of any gas or vapour at* 0° C. *and* 760 *mm. pressure is known as the* **gram-molecular volume.**

On the hydrogen scale this will be the volume occupied at N.T.P. by exactly 2 grms. of hydrogen. This is found to be 22·22 litres.

On the oxygen scale it will be the volume occupied at N.T.P. by exactly 32 grms. of oxygen (or 2·016 grms. of hydrogen). This is found to be 22·4 litres.

In future, we shall adopt the oxygen scale throughout.

Use of the Gram-molecular Volume (G.M.V.).—From the above definition, it is evident that the weight of any gas or vapour which occupies 22·4 litres at N.T.P. will be equal to the molecular weight of the substance measured in grams. It will be found convenient, in most cases involving calculation of molecular weights from gaseous densities, to proceed in this manner, *e.g* :

Given that 260 c.c. of a gas X, measured at 15° C. and 740 mm., are found to weigh 0·471 grm., find the molecular weight of X.

The volume of the gas at N.T.P. is

$$260 \times \frac{273}{288} \times \frac{740}{760} = 240 \text{ c.c.}$$

240 c.c. of X measured at N.T.P. weigh 0·471 grm.

So 22,400 c.c. of X measured at N.T.P. weigh

$$\frac{22400}{240} \times 0{\cdot}471 = 44 \text{ grms.}$$

Hence molecular weight of X = 44.

(The vapour density will of course be half this, *i.e.* 22.)

EXPERIMENTAL METHODS

Densities of Gases.

Principle.—A glass globe is evacuated and weighed. It is then filled with the gas at a known temperature and pressure, and weighed again. The volume of the globe is determined by filling it with water and reweighing.

From the results, the weight of the gas occupying (say) 1 litre at N.T.P. can readily be found; or, if desired, two experiments may be performed, using hydrogen gas in the second instance. The vapour density of the gas (referred to hydrogen) can then be directly calculated.

Precautions and Corrections.—Though the above experiment is exceedingly simple in principle, many precautions have to be taken if accurate results are to be obtained. These cannot be given here in detail (see any text-book of physics for an account of Regnault's work); some, however, may be mentioned.

Weight of the air displaced by the globe.—This will evidently vary with the temperature, pressure, and degree of humidity of the atmosphere. Further, the glass surface of the globe will always carry a film of moisture, the weight of which will also vary with the humidity of the air. To eliminate these factors, two globes, as nearly identical as possible, may be used. Both globes are suspended from the arms of a balance, the suspending wires passing through two holes into a chamber which is kept closed during the weighing, and in which the globes are contained. One of the globes acts merely as a dummy, the determinations of differences of weight, due to the weight of the gas in the other globe, being effected by adding or removing weights from the balance pan in the usual way.

Alteration in volume of the globe.—Lord Rayleigh pointed out that owing to the pressure of the atmosphere upon the evacuated globe, the latter will diminish slightly in volume. This necessary correction was applied by him, by Morley (see reference at end of Chap. V (B)), and by others. The magnitude of the correction can be estimated by placing the globe in a closed cylinder full of water, which is connected to a graduated tube containing mercury. On exhausting the

globe, the change of volume can be measured by the movement of the mercury in the graduated tube.

"Normal Densities."—When work of the highest order of accuracy is being considered, it becomes necessary to define strictly the conditions under which the density of a gas is measured. Owing to the variations in the intensity of the earth's gravitational field, the magnitude of the pressure exerted by a column of mercury 760 mm. high will be different in different latitudes. The definition of the "normal density" of a gas is as follows:

The weight, in grams, of 1 litre (1000·027 c.c.) of the gas, measured at 0° C., under a pressure of 760 mm. of mercury, at sea-level, and latitude 45°.

Accurate Molecular Weight from "Limiting Densities."—If Avogadro's hypothesis were exactly true, it should be possible, by sufficiently careful determinations of gaseous density, to determine molecular weights accurately in this way. Actually, however, equal volumes of gases, measured at the same temperature and pressure, do *not* contain precisely equal numbers of molecules. The reason for this is not that there is a basic error in Avogadro's hypothesis (which would, of course, stultify the whole system of atomic weight determinations which has been so carefully built up), but that real gases do not obey Boyle's law with exactitude. If we took, say, 2·016 grms. of hydrogen, and 44·0 grms. of carbon dioxide, both at very low pressure, we should find that the volumes they occupied at the same temperature were almost exactly equal. But on compressing the gases until their pressure became equal to 1 atmosphere, we should find that the volume of the carbon dioxide diminished somewhat more rapidly than that of the hydrogen. At 0° C. and 760 mm., the volume occupied by the hydrogen would be 22·44 litres, and that occupied by the carbon dioxide 22·24 litres.

Hence, owing to this difference in the compressibility of different gases, equal volumes of gases under the same conditions of temperature and pressure will contain slightly different numbers of molecules, more compressible gases containing a larger number than less compressible gases. The ratio of the normal densities of gases, however accurately

determined, will therefore not give us the exact ratio of their molecular weights, since we are comparing the weights of different numbers of molecules.

(This does not, of course, affect the statement that the molecular weights of gases are equal to twice their vapour densities; the statement remains *approximately* true, and, as we saw in the Introduction to this section, it is in general sufficient to know the approximate molecular weight of an element or compound, provided we know with accuracy its percentage composition, and the atomic weights of the elements concerned.*)

It is, however, possible to correct for this difference of compressibility; and in certain cases very accurate determinations of molecular weight have been made by measuring gaseous densities. We shall consider the method in outline; for precise figures, see *e.g. A Text-Book of Inorganic Chemistry* (Partington).

If W grams of a gas occupy v litres at 0° C. and a pressure p atmospheres, its density in grams per litre at the pressure and temperature considered will be

$$\frac{W}{v}.$$

Let us denote by D the *density per unit pressure* of the gas; then

$$D = \frac{W}{pv}.$$

If Boyle's law were obeyed, D would be independent of p, since pv is constant at a given temperature according to this law.

When $p = 1$ atmos., D is equal to the *normal density* of the gas. When p tends towards zero, D is known as the *limiting density*; and since at very low pressures Boyle's law is obeyed by all gases (the agreement with the law becoming more exact, the lower the pressure), *the ratio of the limiting densities of two gases will be also the ratio of the weights of their molecules.*

Let p_1, v_1, D_1, represent the values of p, v, and D when

* See pp. 207-209.

$p = 1$ atmos.; and p_0, v_0, D_0, their respective values when p tends to zero. Then

$$D_0 = \frac{W}{p_0 v_0} = \frac{W}{p_1 v_1} \times \frac{p_1 v_1}{p_0 v_0}$$
$$= D_1 \times \frac{p_1 v_1}{p_0 v_0} = \text{normal density} \times \frac{p_1 v_1}{p_0 v_0}.$$

D_1 can be found by an accurate determination of the density of the gas at pressures and temperatures not far removed from 760 mm. and 0° C.; $p_0 v_0$ can be found by determining the value of the product pv at various pressures, plotting pv against p on a graph, and extrapolating to zero pressure. This graph will also give $p_1 v_1$ (value of pv when $p = 1$ atmos.).

Use of Accurate Gaseous Densities.—Morley, in the course of the work to which reference has already been made, determined the normal densities of hydrogen and oxygen, obtaining the values

Normal density of hydrogen
$= 0{\cdot}089873 \pm 0{\cdot}0000027$ grm./litre.
Normal density of oxygen $= 1{\cdot}42900 \pm 0{\cdot}000034$ grm./litre.

He determined the volumetric composition of water by exploding together carefully purified hydrogen and oxygen; after applying certain corrections, he obtained the ratio

Volume of hydrogen combining : vol. of oxygen $= 2{\cdot}00269 : 1$.

Later (1915) Burt and Edgar repeated the experiment with still greater accuracy. The gases were measured at 0° C. and approximately 1 atm. pressure. Slightly more than 2 volumes of hydrogen were sparked with 1 volume of oxygen, the latter being gradually introduced; the water formed was frozen by a mixture of solid carbon dioxide and acetone, and the volume of the residual hydrogen measured (for further details, see Partington, *loc. cit.*). They obtained the result

Volume of hydrogen combining : vol. of oxygen $= 2{\cdot}00288 : 1$.

Using Morley's values for the normal densities of the two gases, we find

Weight of hydrogen combining : weight of oxygen
$= 1 : 7{\cdot}9387$.

It is interesting to compare this with the value which Morley obtained by a different method. In another series of experiments, Morley synthesised water in a previously evacuated vessel ; the water was then frozen, and the residual gases pumped out and analysed. He measured the weights of hydrogen and oxygen introduced into the apparatus, the weights of the residual gases, and also the weight of the water, thus checking the accuracy of the experiment (see Chap. V (B)). The mean of 12 experiments gave the result

$$\text{Weight of hydrogen combining : weight of oxygen} = 1 : 7{\cdot}9396.$$

In Morley's former series of experiments, the ratio obtained was 1 : 7·9395.

Atomic Weight of Chlorine.—Gray and Burt (*Trans. Chem. Soc.*, 1909) determined the values of pv for oxygen and hydrogen chloride between pressures of 800 and 150 mm., and thence determined the limiting density of the latter gas. They obtained the value 1·62698. From the relationship

$$\text{Molecular weight of HCl} = \frac{2 \times \text{limiting density of HCl}}{\text{limiting density of hydrogen}},$$

the value 36·186 was obtained. Subtracting 1 from this, we find

$$\text{Atomic weight of chlorine } (H = 1) = 35{\cdot}186,$$

a value in excellent agreement with the most trustworthy results obtained by other methods.*

Correction of the Gram-molecular Volume.—If we divide the molecular weight of a gas by its limiting density, we obtain the volume which would be occupied at N.T.P. by a gram-molecule of an *ideal* gas (*i.e.* one which obeyed Boyle's law exactly). This volume is found to be 22·412 litres.

* This can, of course, be corrected to the standard O = 16 by using the previously determined ratio of combining weights of hydrogen to oxygen.

The Vapour Densities of Volatile Compounds.—In the remainder of this chapter we shall consider briefly the usual methods of determining the vapour densities of volatile substances, within the limits of error normally reached in ordinary experimental work.

Hofmann's Method.—This method consists of introducing a weighed quantity of the volatile substance into the Torricellian vacuum at the top of a barometer tube (Fig. 5).

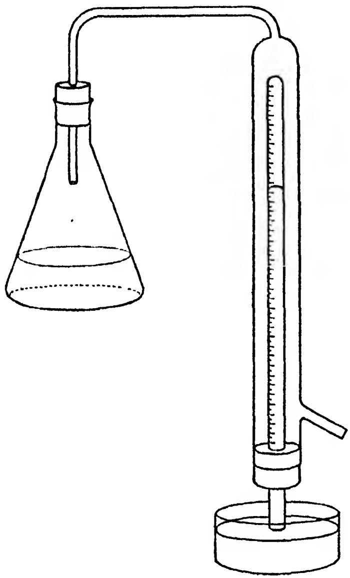

FIG. 5.

The tube, sealed at one end, is graduated, filled with mercury, and inverted in a vessel containing mercury. The greater portion of the tube is surrounded with a jacket, through which the vapour of a liquid boiling at a known constant temperature is passed. A small bulb with a ground glass stopper is weighed, filled with the liquid under examination, and weighed again. It is then introduced into the tube; it rises to the top, the stopper is forced out by the pressure of the vapour within the bulb, and the mercury falls to a certain level, which is noted.

The temperature of the vapour in the tube is that of the jacket. The volume occupied by the vapour is measured directly by means of the graduations on the tube. The atmospheric pressure, minus the *difference* in level of the mercury at the beginning and end of the experiment, gives the pressure to which the vapour is subjected. Hence the vapour density of the substance can be found, since we know the weight of the vapour, and its volume, pressure, and temperature.

Corrections to be applied.

(1) Temperature of the jacket.

If the barometric pressure differs much from 760 mm., the boiling point of the liquid used to heat the jacket must be found from tables.

(2) Temperature of the mercury in the column.

For accurate work, the height of the heated mercury in the barometer tube must be corrected to 0° C. The vapour pressure of mercury at the temperature of the jacket may also be subtracted from the pressure of the vapour.

For most purposes, correction (2) need not be applied.

Advantages of the Method.—Hofmann's method is not much used, but it has two advantages which may be important in certain cases:

(*a*) A small quantity of substance only is necessary.

(*b*) Since volatilisation takes place under reduced pressure, steam may often be used for the jacket when the normal boiling point of the liquid examined lies well above 100° C. Also, the vapour densities of certain substances which decompose to some extent when vaporised under normal atmospheric pressure may sometimes be found by this method.

Dumas' Method.—This method consists of weighing a glass bulb, partially filling it with the volatile substance, heating it in a constant temperature bath until the bulb is completely filled with the vapour and all the liquid has volatilised, sealing the bulb, cooling, and weighing again. The bulb is then opened under water, which rushes in and should fill the bulb completely. The latter is then weighed once more, and the volume of the bulb found from the weight of water which has entered.

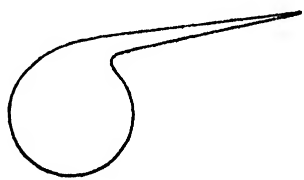

Fig. 6.

The shape of the bulb employed is illustrated in Fig. 6.

The calculation is performed as follows:

Let the weight of the empty bulb in air be W_1 grms.

From the volume of the bulb, and the known pressure and temperature of the atmosphere, the weight of air filling the bulb at the room temperature and pressure can be found. Let this be x grms.

Then the weight of the bulb, if evacuated and sealed, and weighed in air would be $W_1 - x$ grms.

Let the weight of the sealed bulb, containing vapour, and cooled to the temperature of the room, be W_2 grms.

Then the weight of the vapour in the bulb will be

$$W_2 - (W_1 - x) \text{ grms.}$$

Let v c.c. be the volume of the bulb.

Then v c.c. of vapour, at the pressure of the atmosphere, and the temperature of the bath, will weigh $W_2 - (W_1 - x)$ grms.

From this the vapour density may be calculated.

Example.—Find the molecular weight of benzene from the following data:

Weight of empty globe in air = 24·156 grms.
Weight of globe, after sealing and cooling = 24·337 grms.
Volume of bulb = 156 c.c.
Pressure of atmosphere = 740 mm.
Temperature of bath = 120° C.
Temperature of room = 15° C.
Weight of 156 c.c. of air at 15° C. and 740 mm. = 0·186 grm.

Hence weight of evacuated bulb in air

$$= 24{\cdot}156 - 0{\cdot}186 \text{ grms.}$$

Hence 156 c.c. of vapour, at 120° C. and 740 mm., weigh

$$24{\cdot}337 - (24{\cdot}156 - 0{\cdot}186) \text{ grms.} = 0{\cdot}367 \text{ grm.}$$

This volume of vapour, reduced to N.T.P., becomes 105·5 c.c.

Hence 105·5 c.c. of vapour at N.T.P. would weigh 0·367 grm., and 22,400 c.c. would weigh 77·8 grms.

This is the molecular weight of benzene; its vapour density would be $77{\cdot}8/2 = 38{\cdot}9$.

Advantages and Disadvantages of the Method.—Dumas' method may be used for determinations at comparatively high temperatures. This was done, for example, by Deville and Troost, who used globes of porcelain, heated in the vapours of various substances boiling at temperatures up to

918° C. (boiling zinc). The globe was sealed off with an oxy-hydrogen blow-pipe, and a second globe, filled with iodine, the vapour of which progressively dissociates into atoms at high temperatures, was placed in the bath. By calculating the resulting composition of the iodine vapour (already measured over a range of high temperatures) the temperature reached by the globes was found with fair accuracy.

The method can be used for substances which attack mercury.

Disadvantages of the method include the following:

The difficulty of regulating the temperature of the bath exactly (not a very serious drawback).

It cannot be used for substances which decompose on vaporisation at atmospheric pressure.

A large quantity of the substance must be introduced into the bulb in order to displace all the air in it.

If the substance contains a small percentage of an impurity of higher boiling point, the latter will vaporise last, and cause the observed density to be too high.

On opening the bulb under water, a small air-bubble often remains. In work of great accuracy, the volume of this bubble must be allowed for; a correction will also be necessary for the thermal expansion of the bulb.

Victor Meyer's Method.—This is perhaps the commonest method in use.

A long glass tube, with an elongated bulb at the end, is closed with a rubber stopper and heated in the vapour of a boiling liquid. A side tube leads out of the main tube and dips under water (Fig. 7). The heating should continue until no more bubbles or air emerge from the side tube.

Meanwhile a small glass vessel with a ground glass stopper is weighed, filled with the liquid under examination, and weighed again.

As soon as the heated tube has reached a steady state, the rubber stopper is removed, the weighed bottle dropped in, and the stopper immediately closed. (It is advisable to place a little sand at the bottom of the tube to prevent fracture.) The liquid vaporises, forcing out the stopper of the bottle,

and displacing air, which passes through the side tube, and is collected in a graduated tube filled with water. When the displacement has ceased, the graduated tube is levelled in a cylinder of water, and the volume of air read. This volume is then corrected to N.T.P.

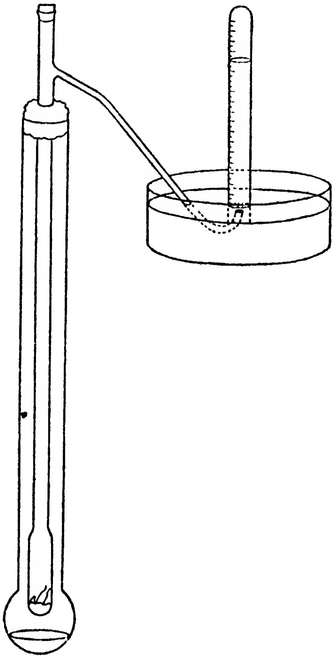

FIG. 7.

The principle of the experiment is this :

On vaporising, the liquid displaces a volume of air equal to the volume of vapour. Since all gases and vapours expand and contract equally with respect to temperature and pressure, the volume of air collected in the graduated tube represents the volume which the vapour of the substance *would have occupied* under these conditions of temperature and pressure, were the substance capable of existing as a vapour under these conditions.

An example will make this clear.

In a Victor Meyer determination of the vapour density of acetone, the following results were obtained :

Weight of glass vessel	= 2·615 grms.
Weight of vessel + acetone	= 2·760 grms.
Weight of acetone	= 0·145 grm.
Volume of air displaced	= 60·5 c.c.

Collected over water at 14° C. and 750 mm. pressure.
Vapour pressure of water at 14° C. = 12 mm.

$$\text{Volume of air at N.T.P.} = 60{\cdot}5 \times \frac{273}{287} \times \frac{738}{760} = 55{\cdot}9 \text{ c.c.}$$

This is the volume which the acetone vapour would occupy at N.T.P., were this substance capable of existing as vapour under these conditions. Hence 22·400 c.c. of acetone vapour at N.T.P. would weigh

$$\frac{0 \cdot 145 \times 22{,}400}{55 \cdot 8} = 58 \cdot 1 \text{ grms.}$$

Therefore molecular weight of acetone = 58.

Advantages of the Method.—Victor Meyer's method gives results which are usually accurate enough to decide the molecular weight of a compound of which the empirical formula is known (*cf.* p. 208). Determinations by this method are performed much more quickly and easily than by Hofmann's or Dumas' methods.

Substances which can be used for the vapour bath include water, β-naphthol (b.pt. 288° C.), and lead (b.pt. 1525° C.; in the latter case the main tube must be of a suitable metal).

Delicate adaptations of Victor Meyer's method have been made by Nilson and Pettersson, Nernst, and others, using small bulbs filled with argon or other inert gases instead of air, and weighing small quantities of the substance under examination on a micro-balance. Nernst, using an iridium bulb, worked at temperatures up to 2000° C., weighing out minute quantities of substance on a balance sensitive to 1/2000 of a milligram.

Exercises on Chapter XVII

(Atomic weights may be taken to the nearest whole numbers, O = 16.)

1. In a determination of the vapour density of stannic chloride by Hofmann's method, the following results were obtained:

Weight of chloride taken	= 0·0420 grm.
Volume of vapour obtained	= 17·2 c.c.
Temperature of jacket	= 100° C.
Barometric pressure	= 758 mm.
Height of mercury column	= 540 mm.

Calculate the molecular weight of stannic chloride (the correction for the thermal expansion of the mercury may be neglected).

2. Find the molecular weight of acetone from the following results obtained in a Dumas experiment:

Weight of open globe in air	= 24·645 grms.
Weight of sealed bulb in air (at end of expt.)	= 24·705 grms.
Volume of bulb	= 70·0 c.c.
Temperature of bath	= 65° C.
Temperature of room	= 15° C.
Pressure of atmosphere	= 750 mm.

(1 c.c. of air, at 0° C. and 760 mm. weighs 0·001293 grm.)

3. In a Victor Meyer determination, 0·064 grm. of propyl alcohol displaced 25·9 c.c. of air, measured over water at 15° C. and 757 mm. pressure.

Find the molecular weight of the alcohol. (Pressure of water vapour at 15° C. = 13 mm.).

4. An organic compound is found to contain 48·65 per cent. of carbon and 8·11 per cent. of hydrogen, the rest being oxygen.

A Victor Meyer determination gave the following result: 0·102 grm. of the compound displaced 34·2 c.c. of air, measured over water at 14° C. and 750 mm. pressure.

Find the molecular formula of the compound. (V. p. of water at 14° C. = 12 mm.)

5. An organic compound contains 37·5 per cent. of carbon and 12·5 per cent. of hydrogen (rest oxygen).

A Victor Meyer determination indicated that the vapour density lay between 31 and 33.

Find the molecular formula of the compound.

6. 0·1564 grm. of an organic compound gave, on combustion, 0·3128 grm. of carbon dioxide and 0·1280 grm. of water, and no other products.

In a Victor Meyer experiment, 0·0885 grm. of the compound displaced 24·3 c.c. of air, collected over water at 12° C. and 746 mm.

Find the molecular formula of the compound. (V. p. of water at 12° C. = 11 mm.)

7. An organic compound is found to contain 85 per cent. of bromine.

In a Victor Meyer determination, 0·193 grm. of the compound displaced 24·7 c.c. of air, measured over water at 13° C. and 753 mm. pressure.

How many atoms of bromine does the molecule contain? (Br = 80; vapour pressure of water at 13° C. = 11 mm.)

CHAPTER XVIII

THE DETERMINATION OF MOLECULAR WEIGHTS FROM THE PROPERTIES OF DILUTE SOLUTIONS

It has long been known that water holding non-volatile substances in solution boils at a higher temperature than pure water. The immediate cause of this is the lowering of the vapour pressure of water by the solution in it of a non-volatile solute. A liquid boils when its vapour pressure is equal to the external pressure. Hence, if the vapour pressure be lowered by the addition of a solute, the solution has to be raised to a higher temperature than before in order to reach the boiling point.

A number of investigations were made on this phenomenon by Faraday, von Babo and others early in the nineteenth century, but the first to yield fruitful generalisations were those of Raoult. Raoult used principally aqueous solutions of organic substances such as cane-sugar, glucose, tartaric acid, citric acid and urea; and non-aqueous solvents such as ether were also employed, choosing as solutes comparatively non-volatile organic compounds (naphthalene, anthracene, etc.), or certain inorganic salts, such as antimony chloride, which are soluble in organic liquids.

The molecular weights of the solvents and solutes were already known with fair certainty from chemical considerations and vapour density measurements; and with this knowledge, Raoult was able to establish a number of very important relationships between the concentration of a solution, the molecular weight of the solute,

and the physical properties of the solution. These relationships were established empirically; we shall first consider them separately, and then show from quite simple considerations that they are in fact inter-related.

The Lowering of Vapour Pressure.—Raoult (1884–1886) established the following generalisations, the third of which is commonly known as "Raoult's Law":

(1) *With a given solvent and a given solute, the relative lowering of vapour pressure is directly proportional to the concentration of the solution.* (This, and the other simple relationships which follow, do not hold good when the solutions are very concentrated; it will be assumed throughout that we are dealing with dilute solutions.)

By "relative lowering" is meant the actual lowering of the vapour pressure divided by the vapour pressure of the pure solvent. Thus if P be the vapour pressure of the pure solvent, and ΔP the lowering of the vapour pressure, the relative lowering is

$$\frac{\Delta P}{P}.$$

The concentration of the solution may be measured in any suitable units; we shall suppose that it is measured in grams of solute per 100 grms. of solvent. If c be the concentration, the above generalisation may be written

$$\frac{\Delta P}{P} = kc, \text{ where } k \text{ is a constant} \quad . \quad . \quad (1)$$

(2) *With a given solvent, the molecular lowering of vapour pressure is independent of the solute.*

By "molecular lowering of vapour pressure" is meant the relative lowering which is produced by dissolving 1 gram-molecule of solute in 100 grms. of solvent. Such a solution would, of course, be very concentrated; actually, the molecular lowering is found by determining the relative lowering in a dilute solution, and then using equation (1).

Raoult's second law states that

$$\frac{\Delta P}{P} \times \frac{m}{c} = K \quad . \quad . \quad . \quad . \quad (2)$$

where

m = the molecular weight of the solute,
c = the concentration of the solution, in grams of solute per 100 grms. of solvent,
K = a constant depending only on the solvent.

If C = the concentration of the solution, in *gram-molecules* of solute per 100 grms. of solvent (the " molecular concentration "),

then

$C = \frac{c}{m}$, and it follows from equation (2) that

$$\frac{\Delta P}{P} = KC \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

Raoult's second law may consequently be expressed as follows:

The relative lowering of vapour pressure of a solvent is directly proportional to the molecular concentration of the solution, the constant of proportionality depending only on the solvent.

(3) *In any dilute solution the relative lowering of the vapour pressure of the solvent is equal to the ratio of the number of molecules of solute present to the total number of molecules of solute + solvent.*

That is,

$$\frac{\Delta P}{P} = \frac{n}{n + N} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where

n = number of molecules of solute,
N = number of molecules of solvent.

Equation (3) may readily be written in terms of concentrations and molecular weights. In solving numerical

problems, however, it is advisable to proceed from first principles, using the equation in the form given above.

Very Dilute Solutions.—When the solution is very dilute, the ratio

$$\frac{n}{n+N} = \frac{n}{N} \text{ approx.}$$

Hence, for such solutions,

$$\frac{\Delta P}{P} = \frac{n}{N} \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

This may be written

$$\frac{\Delta P}{P} = \frac{c}{m} \div \frac{100}{M} = kc,$$

where

c = concentration of solution, in grams solute per 100 grms. solvent,
m = molecular weight of solute,
M = molecular weight of solvent,
k is a constant.

This is identical with equation (1).

Writing C for the concentration of the solution, in gram-molecules of solute per 100 grms. of solvent $\left(i.e.\text{ substituting C for } \frac{c}{M}\right)$, this equation becomes

$$\frac{\Delta P}{P} = C \div \frac{100}{M} = KC,$$

where K is a constant depending only on the solvent. This is identical with equation (2*a*).

Thus equations (1), (2), and (2*a*) may be deduced from (3), as approximations becoming fairly accurate when sufficiently dilute solutions are considered.*

The Raising of the Boiling Point.—This phenomenon was studied by Raoult, and also by Beckmann,

* See also equation (6), p. 237.

who published accurate results in 1889. The very simple law which followed from these may be written

$$\Delta T = K''C \quad . \quad . \quad . \quad . \quad (4)$$

where ΔT is the elevation of the boiling point (degrees C.),

C is the molecular concentration (in gram-molecules of solute per 100 grms. of solvent),

K'' is a constant, depending only on the solvent.

The Lowering of the Freezing Point.—The equation is identical with (4), the only difference lying in the numerical value of the constant ; *i.e.*

$$\Delta T = K'''C \quad . \quad . \quad . \quad . \quad (5)$$

where

T is the lowering of the freezing point (degrees C.),

C is the molecular concentration (in gram-molecules of solute per 100 grms. of solvent),

K''' is a constant, depending only on the solvent.

Raoult, in 1884, published the results of a vast number of experiments on the freezing points of solutions. They included the following :

Solvent.	Number of Solutes employed.
Water	77
Acetic acid	59
Formic acid	10
Benzene	51
Nitrobenzene	18
Ethylene dibromide	7

For each solvent, the value of K''' was found from equation (5), the molecular weights of the solutes being known independently. The following is a summary of the results obtained :

(a) *Non-aqueous Solutions.*—The large majority of substances gave depressions of the freezing point agreeing with equation (5), the value of K‴ depending only on the solvent. A certain number, however, gave abnormally small depressions; usually these were about half the calculated value (*i.e.* that obtained by using K‴ calculated from the majority of solutes).

(b) *Aqueous Solutions.*—Many organic solutes gave normal values; 26 out of the 77 solutes gave values of K‴ ranging between 19·6 and 16·3, the mean being about 19. A few substances, such as phenol and aniline, gave abnormally small depressions; but inorganic salts, acids, and alkalis gave depressions much larger than the normal.

We are not concerned here with these abnormal values; they have been accounted for by supposing the solute to associate into double (or triple, etc.) molecules (giving abnormally small depressions) or to dissociate into "ions" (giving abnormally large depressions).

It may be taken as demonstrated that equation (5) holds good for most dilute solutions in non-aqueous solvents, and for dilute aqueous solutions of many organic substances.

Some values of K″ and K‴ in equations (4) and (5) will be found on p. 254.

The Relationship between Lowering of Vapour Pressure, Elevation of Boiling Point, and Lowering of Freezing Point in Dilute Solutions.

"Phases."—As this term will be useful in the following discussion, it may be defined here.

A phase is a portion of a system which is separated from another portion by a finite boundary at which an abrupt change of physical properties occurs. For example, consider the system water–water vapour in equilibrium. Equilibrium has been aptly described as "a state independent of time"; to continue with this

particular example, we know that if a vessel containing water be placed in a closed chamber at a constant temperature, equilibrium will soon be set up between the water and the water vapour which will be formed in the space above it. In this system there are two phases: a liquid phase (water) and a gaseous phase (water vapour); these phases are separated by a boundary, namely, the surface of the water, at which an abrupt change of physical properties, from liquid to gas or vapour, occurs. The pressure of the vapour will remain constant, as long as the temperature does not alter.

(Those who have studied the Phase Rule will know that in this one-component system $P = 2$, and hence $F = 1$; the system is univariant, and if the temperature is fixed, the pressure must also have a constant value if the two phases are to remain in equilibrium.)

By plotting on a graph the pressures and temperatures at which water and water vapour can exist together in equilibrium, the "vapour pressure curve" of water is obtained. This is represented in Fig. 8 by the curve OA.

OB is a similar curve representing the pressures and temperatures at which ice is in equilibrium with vapour (the diagram is not drawn to scale).

The two curves touch at O. At this temperature, ice and water have the same vapour pressure; and the three phases—ice, water, and water vapour—can only exist in equilibrium at the particular pressure and temperature given by the point O.

(For a system of one component and three phases, $F = O$; the system is non-variant, and alteration of either pressure or temperature will cause the disappearance of one of the phases.)

Finally, the curve OC represents the pressures and temperatures at which ice and water are in equilibrium, vapour being absent. Since ice is less dense than water,

the curve slopes upwards towards the pressure axis; this follows from the general principles of equilibrium (Le Chatelier's theorem).

Triple Point and Freezing Point.—Since three phases are in equilibrium at O, this point is known as a "triple point." The temperature at the triple point is not

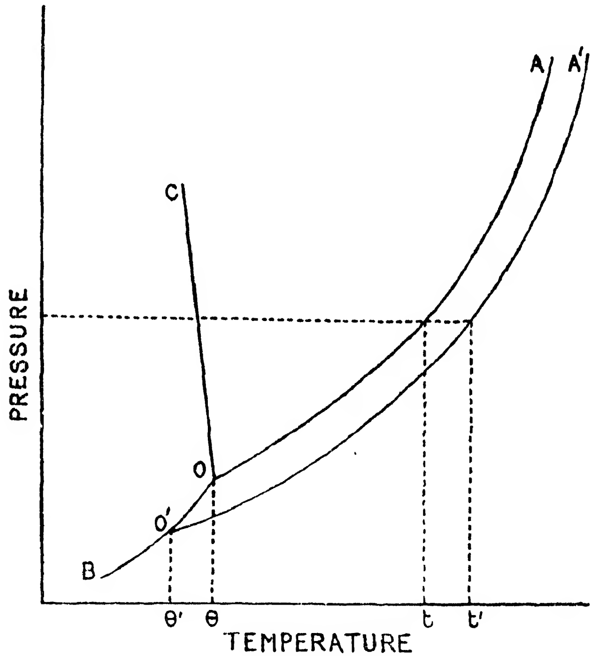

Fig. 8.

exactly the same as that of the freezing point of water. The latter is defined as the temperature at which ice and ice water are in equilibrium *under an external pressure of one atmosphere*. The temperature at the triple point is that at which ice and water are in equilibrium *under their own vapour pressure*. Hence, the temperature of the

triple point will be slightly higher, for the reasons given in the previous paragraph, than the freezing point of water. The actual figures are:

	External Pressure.	Temperature.
Freezing Point	1 atmosphere	0°C. (by definition).
Triple Point	4 mm.	+ 0·007° C.

Boiling Point.—The boiling point of a liquid is that temperature at which the vapour pressure of the liquid is equal to the external pressure. The true boiling point of a liquid is that temperature at which the liquid boils when the external pressure is equal to 1 atmosphere. This is given by the temperature t in the diagram (Fig. 8).

In the above introductory discussion, water has been taken owing to its familiarity. The same considerations would, however, apply to any liquid; if, as is commonly the case, the solid phase is denser than the liquid phase, the curve corresponding to OC would slope upwards *away* from the pressure axis, but in other respects the curves would be similar in form.

Since the effect of pressure upon the freezing point is in all cases small, we may consider, as a first approximation, that the freezing point and the temperature at the triple point are identical.

Dilute Solutions.—We have seen that the effect upon a volatile solvent of the addition to it of a non-volatile solute is to lower its vapour pressure. In Fig. 8 the curve O′A′ represents the *vapour-pressure curve of a solution*; that is to say, the pressures and temperatures at which a solution *of a given concentration* is in equilibrium with solvent vapour.

t' will represent the boiling point of the solution at which the pressure = 1 atm. Evidently t' is higher than t.

At the point O′ the phases in equilibrium are solid solvent, solution, and vapour. To a first approximation the temperature, θ', at this point may be regarded as

the freezing point of the solution, just as θ, the temperature at the triple point, may be regarded as the freezing point of the pure solvent.

From the diagram it is evident that the freezing point of the solution is lower than that of the pure solvent.

We may summarise the results as follows :

As a consequence of the lowering of the vapour pressure of a liquid by the solution in it of a non-volatile substance, the boiling point of the solution will be higher, and the freezing point will be lower, than those of the pure liquid.

Quantitative Relationships.—The above statement is qualitative only ; it says nothing regarding the magnitude of the effects observed, and their connection with the concentration of the solution. We shall proceed to show that these are simply related.

We shall take as starting point the relationship found to hold for dilute solutions, namely, that *with a given solvent, the relative lowering of the vapour pressure is directly proportional to the molecular concentration of the solution, being independent of the nature of the solute.*

Using the same notation as before (p. 230), this is expressed by the equation (2*a*),

namely,
$$\frac{\Delta P}{P} = KC,$$

where K is a constant depending only on the solvent, and C is the concentration of the solution, in moles of solute per 100 grms. of solvent.

(It will be remembered that this simple equation applies only to solutions so dilute that the ratio $n/(n + N)$ may be taken as equal to n/N.)

Since for a given solvent P, the vapour pressure is constant at a given temperature, this equation reduces to

$$\Delta P = K'C \quad . \quad . \quad . \quad . \quad (6)$$

where K′ is a constant depending only on the solvent.

This may be expressed in the following words :

With a given solvent at a given temperature, the actual lowering of the vapour pressure is directly proportional to the molecular concentration of the solution, provided the solution be sufficiently dilute.

The Vapour Pressure Curves.—If we consider a very short length of the vapour-pressure curve of a liquid in the neighbourhood of the boiling point, this

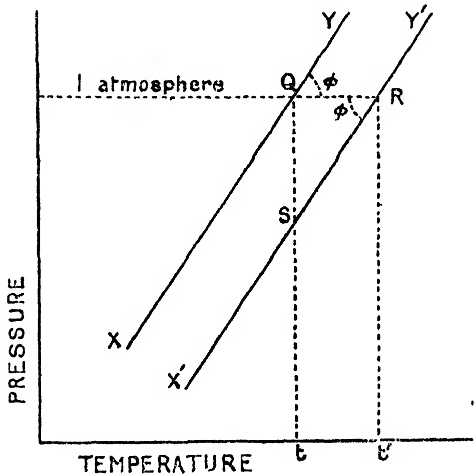

Fig. 9.

portion may be taken to be an approximately straight line.

Similarly a small portion of the vapour-pressure curve of a solution, so dilute that the lowering of the vapour pressure of the solvent is slight, is found by experiment to be *a straight line parallel to the vapour-pressure curve of the pure solvent.*

In Fig. 9, XY and X'Y' represent portions of the vapour-pressure curves of pure solvent and solution

respectively. t is the boiling point of the solvent, t' that of the solution.

Since XY and X′Y′ are parallel, $\angle YQR = \angle QRS = \phi$, say.

Then

$$\frac{QS}{QR} = \tan \phi.$$

But $QS = \Delta P$, the lowering of the vapour pressure of the solvent; and

$QR = \Delta T$, the corresponding elevation of the boiling point.

Hence

$$\Delta T = \frac{\Delta P}{\tan \phi}.$$

ϕ is the slope of the vapour-pressure curve of the pure solvent at the boiling point; and ϕ, and hence $\tan \phi$, will be constant for a given solvent.

Therefore $\Delta T = \text{const.} \times \Delta P$.

But we have seen that $\Delta P = K'C$.

Finally, therefore,

$$\Delta T = K''C,$$

where K'' is a constant depending only on the solvent.

This is identical with equation (4), the relationship found empirically by Raoult.

The calculation with respect to the lowering of freezing point may be carried out on corresponding lines; or, the method of similar triangles may be adopted.

In Fig. 10, p. 240, O represents the triple point for solid solvent, liquid solvent, and vapour. OB is a portion of the vapour-pressure curve for solid solvent, OA the vapour-pressure curve of pure liquid solvent. O′A′, O″A″ are vapour-pressure curves for two solutions.

The lowering of vapour pressure produced at the temperature of the triple point is given by OD, OD′, for the two solutions; the lowering of freezing point is given by O′C,

O″C′. From the principle of similar triangles, it is easy to show that

$$\frac{O'C}{OD} = \frac{O''C'}{OD'}, \text{ or that } \Delta T \text{ is proportional to } \Delta P.$$

The remainder of the proof follows as before.

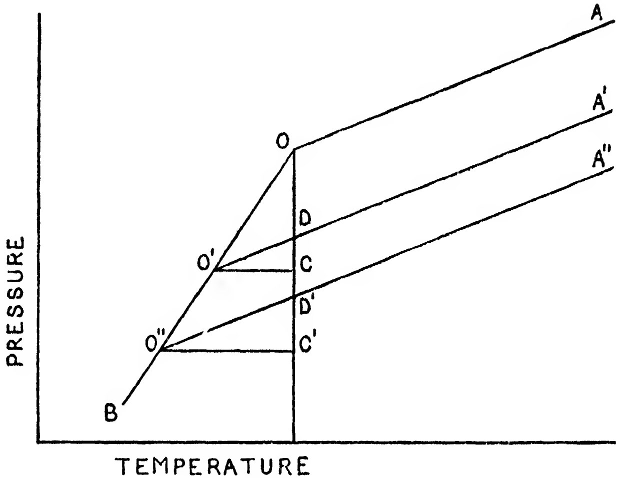

FIG. 10.

The equation obtained is

$$\Delta T = K'''C,$$

which is identical with the empirical equation (5) of Raoult.

SUMMARY

The vapour pressure of a pure liquid is lowered when a non-volatile substance is dissolved in it. From empirical observations, Raoult derived the following law for solutions up to moderate concentrations :

$$\frac{\Delta P}{P} = \frac{n}{n + N} \quad . \quad . \quad . \quad . \quad . \quad (I)$$

where P = the vapour pressure of the pure solvent,
ΔP = the lowering of the vapour pressure,
n = the number of solute molecules present,
N = the number of solvent molecules present.

For dilute solutions, this equation reduces to

$$\frac{\Delta P}{P} = \frac{n}{N} \quad . \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{I}a)$$

With a given solvent at a given temperature, since P is then constant, we have for dilute solutions

$$\Delta P = K'C,$$

where C is the molecular concentration of the solution (measured in gram-molecules per 100 grms. of solvent),
K′ is a constant depending only on the solvent, and independent of the solute.

From a consideration of the vapour-pressure curves of pure solvent, solution, and solid solvent, it is possible to deduce the equations

$$\Delta T = K''C \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{II})$$

where ΔT represents the elevation of the boiling point,
C the molecular concentration,
and K″ is a constant depending only on the solvent;

and one of precisely similar form

$$\Delta T = K'''C \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{III})$$

where ΔT represents the lowering of the freezing point of the solvent,
C the molecular concentration,
and K‴ is a constant depending only on the solvent (its numerical value will of course differ from that of the constant in the preceding equation).

Both these equations were discovered empirically by Raoult, and verified by him for a large number of solvents and solutes. The principal exceptions to the above laws are aqueous solutions of inorganic salts, strong acids, and alkalis.

Experimental Methods

(1) **Lowering of Vapour Pressure.**—Direct determination of vapour pressures is not much used. Raoult attempted to measure the vapour pressures of solutions, using barometer tubes for this purpose, but difficulties due to the presence of traces of air, and evaporation of the solution, with condensation upon the walls of the tube, led him to abandon his experiments.

Certain indirect methods have, however, been used with success; two of these will be described.

Ostwald and Bredig's Method.—Two sets of "potash bulbs," one (A) containing the solution, and the other (B) containing pure solvent, are weighed, and connected together. A slow stream of dry air is then led through the whole apparatus, the air passing first through A and then through B. After a time the current of air is stopped, and the bulbs are again weighed.

The principle of the method may be explained as follows:

Let w = the loss in weight of A,
W = the loss in weight of B,
P = the vapour pressure of the pure solvent at the temperature of the experiment,
ΔP = the lowering of vapour pressure due to the solute.

In A, the air will take up solvent vapour until the latter is present at a partial pressure equal to the vapour pressure of the solution.

Hence, the weight of solvent vapour taken up by a given volume of air will be proportional to $P - \Delta P$.

The air, containing solvent vapour at a partial pressure of $P - \Delta P$, now passes into B, where it takes up a *further* amount of solvent vapour until the partial pressure of the latter becomes equal to P, the vapour pressure of the pure solvent.

Hence, the *additional* weight of solvent vapour taken up by this given volume of air will be proportional to the *difference* between the vapour pressures of the solution and pure solvent, this difference being

$$P - (P - \Delta P), \text{ or } \Delta P.$$

Since the same volume of air passes in turn through A and through B, we have that

$$\frac{w}{W} = \frac{P - \Delta P}{\Delta P} = \frac{\Delta P}{P} - 1.$$

But, from Raoult's equation,

$$\frac{\Delta P}{P} = \frac{n}{n + N},$$

where n = number of solute molecules present, and
N = the number of solvent molecules present,
in the solution.

It is easily seen that

$$\frac{w}{W} = \frac{N}{n}.$$

Knowing the concentration of the solution (in grams of solute per 100 grms. of solvent), and the molecular weight of the solvent, the molecular weight of the solute can be calculated from the observed values of w and W.

Necessary Precautions.—In order to obtain accurate results, the following precautions must be observed :

The temperature of both sets of bulbs must be kept constant throughout the experiment.

The temperature of the air entering A must be the same as that of A.

The stream of air must be sufficiently slow to allow of its saturation with solvent vapour.

The air must be carefully dried.

The first two are ensured by placing both sets of bulbs in a thermostat containing also a coil of lead piping through which the air passes before entering the bulbs.

A suitable rate for the stream of air is about 1 litre an hour ; a second determination may be carried out with a different rate. If the air has been saturated in both cases, concordant results should be obtained.

Barger's Method.—This is a delicate method, for use when only very small quantities of substance are available.

From the equation of Raoult given above, it is evident that two solutions in a given solvent will have the same

vapour pressure when their molecular concentrations are equal (for then the ratio $n/(n + N)$ is the same in both cases, and P is constant for a given solvent at a given temperature).

The method consists in preparing two solutions, one of the substance of which the molecular weight is to be determined, and the other of a substance of known molecular weight. A series of drops of each solution is placed, alternately, in a capillary tube, which is then closed. The sizes of the drops are measured by a travelling microscope. If one solution has a higher vapour pressure than the other, it will partially evaporate; the drops of this solution will decrease in size, and those of the other will increase. The relative concentrations of the solutions are then altered, and further experiments performed until two solutions are found which are in equilibrium. These solutions will then be of equimolecular concentration.

(2) **Elevation of the Boiling Point.**—*Beckmann's Method.*—This method, diagrams of the apparatus of which will be found in any text-book of Physical Chemistry, is very commonly used.

The apparatus consists of a central tube with two side limbs. One of the latter is kept corked, and used for the insertion of a weighed amount of solute; the other is attached to a small reflux condenser. A small piece of platinum wire is sealed through the base of the tube, to assist regular boiling. The lower portion of this central tube is surrounded with a cylindrical glass jacket, also connected to a reflux condenser.

In using the apparatus, some rough garnets or similar objects are placed in the central tube, and a measured quantity of solvent introduced. A "Beckmann thermometer," suitably set, is placed so that the bulb is well covered with liquid.

An arbitrary amount of solvent is placed in the outer jacket (into which glass beads may also be inserted), and the whole apparatus screened from draughts and heated with a very small flame until the liquid is steadily boiling. The boiling point is read on the thermometer, the apparatus allowed to cool somewhat, and a weighed quantity of the solute, the molecular weight of which is to be found, is introduced through the side tube. The boiling point is then read as before, care being taken to see that the solute has completely dissolved.

The principal difficulty of the experiment is to obtain steady boiling, without superheating. The apparatus is designed so as to minimise this superheating, but it will frequently be found that the thermometer registers small fluctuations of temperature. (The thermometer should be tapped before reading.)

The rate of boiling should be as nearly as possible the same for both solvent and solution. If the barometer has shown any marked change during the course of the determinations, a correction must be applied for the consequent alteration of boiling point.

Successive amounts of solute can of course be added through the side tube without disturbing the liquid in the central tube. Suitable quantities to add are such that the boiling point is raised about 0·2 degree by each addition. To prevent the solid from adhering to the sides of the tube before reaching the solvent, the solute may be compressed into small tablets before weighing it out.

Landsberger's Method.—This is a quicker and more convenient method, which may often be used with advantage when results of great accuracy are not required.

It consists in heating the solution with the vapour of the boiling solvent, which is passed into the solution, giving up its latent heat of condensation until the solution is raised to the boiling point. Since, owing to loss of heat from the solution, some vapour will continue to condense after the boiling point has been reached, the solution will gradually become more dilute.

A tube, about the size of a boiling tube, is graduated in c.c., and surrounded with a jacket. Some pure solvent is placed in the tube, a thermometer inserted, and solvent vapour passed in under the surface of the liquid until the thermometer reaches a steady temperature. This is the boiling point of the pure solvent.

A weighed quantity of solute is then added (some of the solvent being removed, if much has condensed), and vapour passed in as before. As soon as the temperature ceases to rise the passage of vapour is stopped. The solution is allowed to cool, and its volume read directly.

(3) **Depression of the Freezing Point.**—A tube, with a side limb for introduction of solute, is jacketed with an outer

tube, a measured amount of solvent placed in it, a thermometer inserted, and the whole immersed in a freezing mixture. The central tube should be provided with a stirrer.

The liquid is stirred ; it will supercool to some extent, and then, on separation of solid, the temperature will rise to the freezing point of the solvent.

A weighed quantity of solute is introduced, the apparatus being removed from the freezing mixture and the liquid stirred until a clear solution is obtained. The freezing point of the solution is then found as before.

As in the boiling point method, successive amounts of solute can be added without removing the liquid from the central tube.

Errors and Precautions.—Too much supercooling must be avoided. If much solid separates the solution will evidently become more concentrated, since it is pure solvent which separates. The temperature of the freezing mixture should not be more than 5 or 6 degrees below the ultimate freezing point of the liquid. Supercooling may be lessened by vigorous stirring ; in some cases it is advisable to insert a *small* crystal of the solid solvent as soon as the temperature of the liquid has fallen one or two degrees below the freezing point.

With hygroscopic solvents, such as acetic acid, care must be taken to see that they are originally pure, and that water is not absorbed during the experiment. The side tube should be kept corked, or connected with a calcium chloride tube.

APPENDIX TO CHAPTER XVIII

OSMOTIC PRESSURE

This remarkable phenomenon may be considered to be the underlying cause of all the effects mentioned in the earlier portion of this chapter. Since, though of very great theoretical importance, the phenomenon in itself is not much used for the purpose of determining molecular weights, it will be only briefly described.

Semi-permeable Membranes.—A number of membranes occur naturally, or may be prepared artificially, which allow of the passage through them of water, but not of substances contained in solution in the water. Among natural membranes may be mentioned certain animal and vegetable tissues, such as pig's bladder, and the walls of plant cells. Artificial membranes include various silicates (utilised in the manufacture of a " chemical garden ") and copper ferrocyanide.

The last-named has been used for many experiments upon osmotic pressure. Owing to its fragility, it should be deposited within the walls of a porous pot. In Morse and Frazer's experiments, the pots were soaked in water, air being removed by evacuation, and then filled with a weak (tenth-molar) solution of copper sulphate. The pot was then placed in a solution of potassium ferrocyanide of equal strength, and an electric current passed from the inside of the pot to the outer solution. The membrane is deposited in the walls of the pot.

Osmosis.—If an aqueous solution be placed inside a vessel, the walls of which consist of a semi-permeable membrane, and the whole immersed in pure water, water will tend to pass into the solution. Pressure will consequently be set up inside the vessel; this is known as *osmotic pressure*. The phenomenon of the passage of the water into the solution is called *osmosis*.

Accurate measurement of osmotic pressure is a matter of difficulty, owing to the high pressures involved, and the frequent rupture of the membranes. In Morse and Frazer's experiments, which were refinements of the early classical work of Pfeffer, cylindrical pots, made from special clays, were used. These were glazed at the open end, and a copper ferrocyanide membrane deposited on the remainder as described. The pot was completely filled with solution, and a mercury gauge tightly clamped to the open end. This gauge consisted of a graduated tube closed at one end, the upper portion of the tube being filled with nitrogen. The compression of the nitrogen produced indicated the pressure which was developed inside the pot.

In experiments conducted by the Earl of Berkeley and Mr. E. G. Hartley, a similar porous cylinder was employed. Pressure was, however, applied to the solution until osmosis

ceased. This has the advantage that the solution does not become diluted during the experiments.

Laws of Osmosis.—The following relationships are found to hold between the osmotic pressure, the temperature, and the concentration of *dilute* solutions :

(*a*) *At a given temperature, the osmotic pressure is directly proportional to the concentration of the solution.* This may be written in a form which brings out the analogy with Boyle's law, namely

$$pv = \text{constant},$$

if by p we denote the osmotic pressure,
v the volume of the solution containing a given weight of solute.

(*b*) *With a solution of a given concentration, the osmotic pressure is directly proportional to the absolute temperature.* This is evidently analogous to Charles's Law, in the form that "at constant volume, the pressure of a gas is proportional to its absolute temperature."

(*c*) Both these statements can be collected in the equation

$$pv = \text{const.} \times \text{T},$$

where T is the absolute temperature.

To complete the analogy, let us denote by V′ the volume of solution (in litres) containing 1 gram-molecule of solute, and by P′ the corresponding osmotic pressure. Then we can write

$$\text{P}'\text{V}' = \text{R}'\text{T}, \text{ where R}' \text{ is a constant},$$

which is analogous to the gas equation

$$\text{PV} = \text{RT},$$

where V here means the volume, in litres, occupied by 1 gram-molecule of gas, at the pressure P atm., and temperature T° Abs.

Value of the Constant.—It is remarkable that R′ has almost the same numerical value as R. This may be shown by some of Berkeley and Hartley's results. For dilute solutions of cane-sugar (up to 100 grms./litre) at 0° C., the mean value of the product P′V′ was 22·6, as compared with 22·4 for a gas.

The analogy between the pressure of an ideal gas, and the osmotic pressure of a dilute solution, is therefore complete.

Use in Molecular Weight Determinations.—It is evident that the relationship just described could be utilised in determinations of molecular weight. A substance which obeyed the osmotic pressure laws would give, at 0° C., an osmotic pressure of 1 atmosphere when 1 gram-molecule of it was dissolved in 22·4 litres of solution.

As an example, we may take the following calculation :

1 grm. of a substance A, dissolved in 1 litre of water, gave an osmotic pressure of 105 mm. of mercury at 30° C.

Calculate the molecular weight of A.

$$105 \text{ mm.} = \frac{105}{760} = 0{\cdot}138 \text{ atm.}$$

An osmotic pressure of 0·138 atm. is given, at 30° C., by 1 grm. of A in 1 litre of solution.

1 grm. of A in 22·4 litres of solution would give, at 0° C., an osmotic pressure of

$$0{\cdot}138 \times \frac{1}{22{\cdot}4} \times \frac{273}{303} = 0{\cdot}00555 \text{ atm.}$$

Hence to produce an osmotic pressure of 1 atm., at 0° C., the weight of A dissolved in 22·4 litres of solution would have to be

$$\frac{1}{0{\cdot}00555} = 180 \text{ grms.}$$

This will, therefore, be the molecular weight of A.

Actually, however, the molecular weight of such a substance could be determined with greater accuracy, and far more easily, by means of one of the methods described earlier in this chapter.

"Abnormal Osmotic Pressures."—Just as with freezing points, etc., we find that certain substances, such as inorganic salts, give abnormally large osmotic pressures. This has been explained by supposing that the molecules of such substances dissociate into charged "ions."

In addition to this, however, it is found that substances such as cane-sugar, which give normal values in dilute solu-

tion, give abnormally large osmotic pressures when the solutions become concentrated. Thus, Berkeley and Hartley found that the osmotic pressure, at 0° C., of a solution containing 750·6 grms. of cane-sugar per litre was 133·74 atmospheres, whereas such a solution, if it had obeyed the equation

$$P'V' = R'T,$$

would have given a pressure of about 50 atmospheres.

One explanation advanced for this is similar to the well-known van der Waals' equation. In order to account for the deviations from the simple gas laws shown by real gases, van der Waals introduced two terms into the gas equation, one taking account of attractions between the molecules, and the other of their finite volume. The modified equation becomes

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT,$$

where $\frac{a}{V^2}$ represents the effect of intermolecular attraction, and b may be taken roughly as depending on the volume occupied by the molecules.

It was found by Sackur (1910) that a simplified form of van der Waals' equation holds good with considerable accuracy for solutions up to high concentrations. Sackur's equation is

$$P'(V' - b) = R'T,$$

where P', V', R', and T have the same significance as before (R' being numerically equal to R), and b is a constant for a given substance at a given temperature.

In this equation, b may therefore be taken as a figure directly connected with the finite volume occupied by the solute molecules, which in concentrated solutions must be considerable.

b was found to decrease rapidly with temperature. This Sackur considered as probably indicating that the solute molecules are hydrated, the degree of hydration diminishing rapidly as the temperature is raised.

Some Theoretical Considerations.—*Relationship between osmotic pressure and lowering of vapour pressure.*

It may be readily shown, in a general way, that these two phenomena are connected.

Suppose a solution be contained in a tube (Fig. 11), closed at one end by a semi-permeable membrane, and open at the other. The former end dips under the surface of pure solvent, the whole being contained in a closed vessel filled with solvent vapour only. Solvent will enter the tube until the osmotic pressure is balanced by the hydrostatic pressure at the base of the tube. A state of equilibrium will finally be reached; and when this is so, there must also be equilibrium between the solution, the pure solvent, and the solvent vapour in the closed vessel.

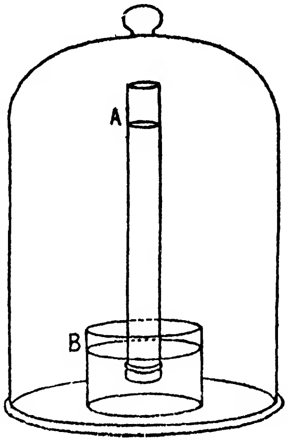

FIG. 11.

The vapour pressure of the solution will be equal to the pressure of solvent vapour at the point A; and that of the pure solvent equal to that of the solvent vapour at the point B.

The pressure of solvent vapour at B will be greater than that at A by an amount equal to the weight of a column of solvent vapour, of unit cross-section, and height AB. Hence, if ΔP be the lowering of vapour pressure of the solvent, due to the presence of solute,

$$\Delta P = hd,$$

where h = the height AB, and
d = the density of the solvent vapour.

d may be taken as sensibly constant; and h will evidently be proportional to the osmotic pressure.

When the solution is dilute, the osmotic pressure is directly proportional to the concentration, c, of the solution.

Hence, under these conditions,

$$\Delta P = Kc,$$

where K is a constant.

This is the relationship found empirically by Raoult for dilute solutions (see p. 237, equation (6)).

Further, it has been shown earlier in this chapter that from this equation we may deduce the equations relating to the raising of the boiling point and the lowering of the freezing point (pp. 238–240).

Hence all these relationships follow from the phenomenon of osmotic pressure.

Application of Thermodynamics.—This is too advanced for full consideration; but the results of the principles of thermodynamics, applied to dilute solutions, are so important and far-reaching that a brief mention of them must be made.

Van't Hoff has shown that the equation

$$P'V' = R'T,$$

where P' = osmotic pressure,
V' = volume of solution containing 1 gram-molecule of solute,
T = absolute temperature,
R' is a constant having the same value as the gas constant,

follows from Henry's law (the law which states that the mass of a gas which dissolves in a given mass of solvent is directly proportional to the partial pressure of the gas over the solution, the temperature being constant).

Though the elementary student need hardly master the proof, it is of great importance that he should understand the principles which underlie it. The assumptions made are these:

(1) Henry's law is accurately obeyed.

(2) The gas is "perfect"; that is, it obeys the equation

$$PV = RT$$

accurately.

(3) The principle which states that when a series of operations are carried out reversibly at constant temperature, and the system is brought back to its original condition (*i.e.* when an "isothermal reversible cycle" has been completed), the nett work done is equal to zero.

Lowering of Vapour Pressure, Elevation of the Boiling Point, Depression of the Freezing Point.

Thermodynamical principles, applied to solutions, lead to equations identical with those found empirically by Raoult.

It is assumed that the osmotic pressure of the dissolved substance obeys the equation

$$P'V' = RT$$

(where R may stand for the constant in either this equation or the gas equation). The remaining assumptions are similar to those given above; in deducing equations (4) and (5) the principle of the "Carnot Cycle," regarding the efficiency of a perfect heat engine, is introduced.

Calculation of the Constants of Molecular Elevation and Depression.

A valuable consequence of the above is that the constant K in the equation

$$\Delta T = KC$$

(where ΔT stands either for the elevation of boiling point or depression of freezing point, and C for the concentration of the solution, in gram-molecules per 100 grms. of solvent), may be calculated from other constants which may be found independently. Raoult, as we have seen, found this law to hold good empirically; knowing the molecular weights of the solutes employed, he calculated the values of K for a given solvent from the observed values of the boiling-point elevation or freezing-point depression. Thermodynamics furnishes us with a second means of evaluating the constant; a means which is in some cases very useful when dealing with solvents for which we have insufficient data to enable the constant to be calculated empirically.

Considering first the equation for the elevation of the boiling point,

$$\Delta T = K''C,$$

thermodynamical reasoning shows that

$$K'' = \frac{RT^2}{100L},$$

where R is the gas constant in calories/deg.

T is the absolute temperature at which the solvent boils, under a pressure of 1 atmosphere,

L is the latent heat of vaporisation of solvent,

C is here measured in gram-molecules per 100 grms. of solvent.

For the depression of the freezing point, an exactly similar expression may be developed,

where T is the freezing point of pure solvent (degrees Abs.),
L is the latent heat of fusion per gram of solvent.

A few values calculated from the above expression are here compared with the values of the constant found empirically.

Ebullioscopic Constant (*i.e.* molecular elevation of the boiling point).

Water.

$R = 2$ calories per degree, approx.,
$T = 373$,
$L = 540$ calories per gram,

whence $K'' = \dfrac{2 \times (373)^2}{100 \times 540} = 5{\cdot}2$ (value observed $= 5{\cdot}2$).

Benzene.

$T = 353$,
$L = 95$ calories per gram,
whence $K'' = 2{\cdot}6$ (value observed $= 2{\cdot}57$).

Cryoscopic Constant (*i.e.* molecular depression of the freezing point).

Water.

$T = 273$.
$L = 80$ calories per gram.
whence $K''' = 18{\cdot}6$ (mean value of many observations, by independent workers, is $18{\cdot}6$).

NOTE.—In doing calculations, care must be taken to see that the concentration is measured in the appropriate units. In many books in which the thermodynamical calculation is given, it will be found that the concentration is measured in gram molecules per cubic centimetre of solution. The expression for the above constants then becomes

$$K = \frac{RT^2}{\rho L},$$

where ρ is the density of the solvent

Occasionally (especially where the elevation of the boiling point is concerned) the concentration may be measured in grams of solute per 1000 grms. of solvent.

Such alteration of units will, of course, affect the numerical value of the constant, and in employing this constant in calculations the student should satisfy himself that he knows which units of concentration have been employed in its evaluation.

In this book, concentrations have been reckoned throughout in gram-molecules of solute per 100 grms. of solvent.

Deviations from the above laws.—For dilute solutions of substances such as cane-sugar, good agreement is obtained between the experimental results and the calculated values. For many aqueous solutions, however, considerable divergence is observed. This divergence is very marked in solutions of inorganic salts, acids, and alkalis (*i.e.* when the solute is an "electrolyte"); and becomes marked with concentrated solutions of non-electrolytes, both in aqueous and non-aqueous solvents.

These discrepancies do not mean that the laws of thermodynamics are unsound, *but that the assumptions made in the calculations are too simple.* To discuss this fully would take us too far; but it is important to realise that this is the fundamental cause of the differences between the values calculated from thermodynamical principles and those which may be actually observed.

Exercises on Chapter XVIII

1. A current of dry air is passed through two potash bulbs in succession, the first containing a solution of 0·825 grm. of a substance X dissolved in 3·124 grms. of ethyl alcohol, and the second containing pure alcohol.

After a certain time the loss in weight of the solution is found to be 0·628 grm., and that of the pure alcohol, 0·0530 grm. Calculate the molecular weight of X.

2. In an experiment by Barger's method, the following solutions were found to be in equilibrium;

(*a*) a solution of 0·245 grm. of methyl oxalate in 2·61 grms. of alcohol;

(*b*) a solution of 0·106 grm. of a substance Y in 1·30 grms. of alcohol.

Calculate the molecular weight of Y.

3. Find the molecular weight of naphthalene from the following data:

Weight of benzene (solvent) = 17·6 grams.
Weights of naphthalene dissolved in the benzene (total weights) = 0·214, 0·437, 0·684 grm.
Corresponding elevations of boiling point = 0·256°, 0·524°, 0·820° C.
Constant of molecular elevation for benzene = 27.

4. 0·8125 grm. of ferric chloride, dissolved in 20 grms. of alcohol, raised the boiling point of the latter by 0·293° C.

Find the molecular weight of ferric chloride. (Mol. const. of elevation for alcohol = 11·7.)

At 444° C. the vapour density of ferric chloride vapour is about 162. What explanation can you suggest for this?

5. The following table gives freezing points of 2 per cent. aqueous solutions of various organic substances:

Acetic acid ($C_2H_4O_2$)	−0·633° C.
Chloral hydrate ($C_2H_3O_2Cl_3$)	−0·228° C.
Lactic acid ($C_3H_6O_3$)	−0·427° C.
Butyric acid ($C_4H_8O_2$)	−0·425° C.

Calculate the mean value obtained for the constant of molecular depression for water.

6. 0·4328 grm. of a carbohydrate gave on combustion 0·6348 grm. of carbon dioxide, and 0·2597 grm. of water.

0·364 grm. of this substance, dissolved in 30 grms. of water, lowered the freezing point of the latter by 0·125° C.

Find the molecular formula of the carbohydrate. (Const. of molecular depression for water = 18·6.)

7. An aromatic hydrocarbon contains 94·38 per cent. of carbon. Solutions of 0·216, 0·348, 0·512 grm. of the hydrocarbon in 12·2 grms. of benzene showed elevations of the boiling point of 0·269°, 0·430°, and 0·638° C. respectively.

Find the molecular formula of the hydrocarbon. (Const. of molecular elevation for benzene = 27.)

8. Calculate the osmotic pressures at 15° C. of 1 per cent. solutions of mannose ($C_6H_{12}O_6$), mannitol ($C_6H_{14}O_6$), and sucrose ($C_{12}H_{22}O_{11}$).

What would be the concentration of a solution of sucrose which had the same osmotic pressure as a 5 per cent. solution of mannose, both being at the same temperature?

9. Calculate the molecular weight of a substance, 0·265 grm. of which, dissolved in 67·4 c.c. of water, gave an osmotic pressure of 206 mm. at 14° C.

10. 0·345 grm. of a sugar, of empirical formula CH_2O, was found to give an osmotic pressure of 688 mm. at 15° C., when dissolved in 50 c.c. of water.

Find the molecular formula of the sugar.

CHAPTER XIX

SOME SPECIAL METHODS OF FINDING MOLECULAR FORMULÆ

THE main principles upon which our knowledge of molecular formulæ is based have now been described. Chemists, however, are at liberty to use any evidence which is forthcoming regarding molecular structure; and a few special methods which have proved of value in certain cases may be briefly discussed.

Molecular Weights by Diffusion.—It is well known that if one gas be introduced into another, it will be found that after a certain lapse of time the gases have become evenly mixed. This mixing is independent of the existence of draughts or convection currents in the gases, though these may hasten the process; it is due to the motion of the individual molecules.

This phenomenon, which is known as diffusion, was investigated by Graham, who used for this purpose a glass tube closed at one end with a plug of plaster of Paris. The tube was filled with mercury, and its open end immersed in a jar also containing mercury. Some of the gas under examination was then admitted to the tube, and its initial volume measured with the mercury standing at the same level inside and outside the tube. Diffusion commenced, the gas in the tube diffusing outwards through the plug, while at the same time air diffused into the tube. During this process, the tube was raised or lowered so as to keep the mercury always at the same level inside and outside the tube. After a time the gas became completely replaced by air, and no further

alteration of volume occurred. The volume of air in the tube was then read.

Let v_1 c.c. be the volume of the gas initially in the tube; and let v_2 c.c. be the volume of air found at the end.

Let t seconds represent the time occupied by the whole experiment.

Then the average rate of diffusion of the first gas will be $\frac{v_1}{t}$ c.c. per second; and the average rate of diffusion of the air will be $\frac{v_2}{t}$ c.c. per second.

Hence

$$\frac{\text{the rate of diffusion of the first gas}}{\text{the rate of diffusion of air}} = \frac{v_1}{v_2}.$$

By comparing the rates of diffusion of different gases of known density, Graham found that the velocity of diffusion of a gas is inversely proportional to the square root of its density ("Graham's Law").

If we suppose that the rate of diffusion of a gas is directly proportional to the mean velocity of its molecules, the kinetic theory of gases leads to the same result. For we have seen (Chap. XV) that with two gases, A and B, at the same temperature and pressure,

$$\tfrac{1}{2}m_A c_A{}^2 = \tfrac{1}{2}m_B c_B{}^2,$$

where m is the mass of the molecule, and c the root mean square velocity (which is approximately the same as the average velocity) of the molecule.

Hence

$$\frac{c_A}{c_B} = \sqrt{\frac{m_B}{m_A}},$$

that is, the velocity of diffusion of a gas will be inversely proportional to the square root of its molecular weight, and hence inversely proportional to the square root of its density, which is Graham's Law.

If, instead of allowing the gas to diffuse through a

porous plug, it is made to stream through a fine hole pierced in a narrow plate, the same relationship is observed. The phenomenon in this case is known as *effusion*. Bunsen devised an apparatus for the study of effusion, consisting of a glass cylinder, drawn out and furnished at one end with a stopcock. This stopcock leads directly to a second tube, across which is fitted a thin platinum plate with a fine hole in the centre. The cylinder is filled with gas, and immersed in a jar of water or other liquid. The stopcock is opened, and the time which the liquid takes to rise a certain distance inside the cylinder is noted. The relative rates of effusion of different gases can thus be compared.

The Molecular Weight of Ozone.—Graham's law was utilised by Soret in determining the molecular weight of ozone. Pure ozone had never been prepared at this time, so that it was impossible to determine its vapour density. The principle of Soret's experiment was as follows:

Two experiments were performed. In the first, ozonised oxygen was allowed to diffuse for a certain time into an equal volume of pure oxygen. Diffusion was then stopped, and the concentration of ozone in the remaining ozonised oxygen, and also that in the oxygen into which the ozone had diffused, were measured by treating equal volumes of the gases with excess of potassium iodide solution, and estimating the iodine liberated with standard sodium thiosulphate.

Suppose the volumes of sodium thiosulphate solution required were v_1, v_2 c.c. respectively. Then we have

$$\frac{\text{volume of ozone diffused}}{\text{total volume of ozone originally present}} = \frac{v_2}{(v_1 + v_2)}.$$

An exactly similar experiment was then performed, using instead of ozonised oxygen a mixture of oxygen and chlorine in suitable proportions. Diffusion was allowed

to proceed for the same length of time as before, and the fraction of the total chlorine which diffused into the oxygen was measured as in the above equation.

The fraction of the gas which has diffused in a given time will be directly proportional to its rate of diffusion. If f, f', are the fractions found for ozone and chlorine respectively, and M is the molecular weight of ozone, then by Graham's law

$$\frac{f}{f'} = \sqrt{\frac{71}{M}}.$$

Soret's figures were

$$\frac{f}{f'} = \frac{0{\cdot}271}{0{\cdot}227}, \text{ whence } M = 50.$$

He also performed a third experiment, using a mixture of oxygen and carbon dioxide. In this case, the carbon dioxide was estimated by shaking the gas with excess of standard baryta water, the excess of baryta being then titrated with standard acid, using phenol-phthalein as indicator. As before, we have (if f'' represents the fraction of carbon dioxide which diffuses in the given time)

$$\frac{f}{f''} = \sqrt{\frac{44}{M}}.$$

The ratio was found to be

$$\frac{0{\cdot}271}{0{\cdot}290}, \text{ whence } M = 50{\cdot}5.$$

The conclusion to be drawn therefore is that ozone is triatomic, with a molecular weight of 48.

Soret's apparatus consisted essentially of two cylinders separated by a sliding glass partition. The upper cylinder was filled with oxygen, and the lower with the mixture of gases under examination. Communication was then made with the cylinders by sliding the partition

until the gases commenced to diffuse through a hole in the partition.

(Besides the determination of molecular weight, with which we are concerned here, Graham's law has been of great service in ascertaining whether or not a given gas is a mixture or a single substance. In this way, the existence of dissociation can be demonstrated in the vapours of ammonium chloride, mercurous chloride, phosphorous pentachloride, and other substances. Again, a mixture of hydrogen and ethane in equal proportions by volume would have the same density as pure methane, and by the explosion method (*vide infra*) would also be indistinguishable from methane. If a portion of the gas were allowed to diffuse, however, it would be found that this portion contained excess of hydrogen.)

The Molecular Weights of Acids.—The molecular weights of weak acids which can be isolated in the pure state may often be found by determining the freezing points of their aqueous solutions, the effect due to ionisation being, with the weaker acids, negligible in solutions of moderate concentration.

A method of very general use lies in the determination of the vapour densities of the ethyl esters of acids. In many cases the free acids decompose partly or completely on vaporisation; but their ethyl esters are usually much more stable. The formula weight of the ethyl group, C_2H_5, is 29; if M be the molecular weight of the ethyl ester, that of the acid will be

$$M + 1 - 29$$

(since each ethyl group replaces one hydrogen atom).

The equivalent weight of an acid is defined as that weight of the acid which contains one equivalent weight of replaceable hydrogen.* Acids which contain only one atom of replaceable hydrogen in the molecule are said to be monobasic; those which contain two, to be dibasic, and

* Equivalent weight of hydrogen = 1·008.

so on. Evidently the molecular weight of an acid will be equal to its equivalent weight multiplied by its basicity.

Acids which can be isolated in the pure state readily lend themselves to a determination of their equivalent weights. All that is necessary is to make up a solution of the acid of known concentration, and to determine the weight of the acid which neutralises one gram-equivalent of a suitable base. With organic acids, the method commonly used is to heat the silver salt of the acid, which usually decomposes to metallic silver. The basicity may often be found by adding to the acid one-half, one-third, etc., of the quantity of base (preferably caustic soda or potash) required for complete neutralisation, concentrating the solution by evaporation, and examining the crystals which separate. An acid of basicity n will usually be found by this method to give n different salts.

NOTE.—This method of determining basicity is not always easy to apply, and in practice the molecular weights of the weaker organic acids would generally be found from freezing point measurements, or from the vapour density of the ethyl ester. If it were required to find the basicity, an independent determination of the equivalent weight would be made (from the silver salt), and the basicity calculated from the relation

$$\text{Basicity} = \frac{\text{Molecular Weight}}{\text{Equivalent Weight}}.$$

"Method of Replacement:"—The principle of this method rests on the argument that if it is possible to replace an element present in a given compound in n stages, there must be at least n atoms of that element in the molecule of the compound.

For example, acetic acid has the empirical formula CH_2O. By passing chlorine into boiling acetic acid in the presence of a little iodine as ' carrier," it is possible to prepare compounds having the empirical formulæ $C_2H_3ClO_2$, $CHClO$, and $C_2HCl_3O_2$. If we double the formula of the second of these compounds, writing it

$C_2H_2Cl_2O_2$, it becomes evident that hydrogen atoms are replaced in three stages. Hence there must be at least three atoms of hydrogen in the molecule of acetic acid, and the *simplest* formula for the molecule must be $C_2H_4O_2$.

Some attempt has been made on these lines to investigate the molecular composition of substances such as starch; beyond indicating that these substances must have very high molecular weights, it cannot be said that the method has proved of very great value.

The white substance formed by the action of nitric acid on tin, known as β-metastannic acid, has been supposed to contain 5 atoms of tin in the molecule, from the fact that the action of concentrated hydrochloric acid upon it produces a substance of the composition $H_8Sn_5O_{13}Cl_2$. The formula of the acid is often written as $H_{10}Sn_5O_{15}$, but some of the water present appears to be merely water of hydration.

Exercises on Chapter XIX

1. 0·652 grm. of an organic acid was dissolved in 100 c.c. of water. 10 c.c. of the solution were found to be equivalent to 11·05 c.c. of $N/10$ caustic soda solution.

The vapour density of the ethyl ester of the acid was found to be approximately 90.

What is the molecular weight, and the basicity, of the acid?

2. 0·4615 grm. of the silver salt of an organic acid gave on ignition a residue of 0·2915 grm. of silver.

0·215 grm. of the acid, dissolved in 40 grms. of water, lowered the freezing point of the latter by 0·532° C.

Find the molecular weight, and basicity, of the acid. (Constant of molecular depression for water = 19.)

3. The silver salt of a weak acid has the following percentage composition: Ag 78·3 per cent., N 10·2 per cent., O 11·5 per cent.

The vapour density of the ethyl ester of the acid = 59.

Find the molecular formula of the acid, and suggest any further experiments which might be made in order to confirm your conclusion.

CHAPTER XX

DETERMINATION OF THE MOLECULAR FORMULÆ OF SOME COMMON COMPOUNDS

THE most general means of determining the molecular formula of a substance consists in finding the gravimetric composition of the substance, and hence deriving its empirical formula ; the molecular weight is then found independently.

In the examples considered in this chapter, the gravimetric composition can often be found by methods not here given, but which can be found on reference to a text-book.

This chapter deals more particularly with certain special methods which may be taken as valuable confirmatory evidence of the molecular formulæ. In any complete discussion, evidence should of course be provided that the given compound consists of the elements concerned, and of no others—for example, that carbon dioxide contains carbon, oxygen, and nothing else. In many of the cases here given, this evidence is provided in the text ; in others, the proof is left to the ingenuity of the student.

If the elementary composition of the gas is known, the vapour density alone may indicate the molecular formula ; for example, if it is known that ammonia consists of nitrogen and hydrogen only, and has a vapour density of 8·5, the resulting molecular weight of 17 indicates that the molecular formula is NH_3 ; but confirmatory evidence is desirable.

(In the examples which follow, the arguments based on Avogadro's hypothesis are sometimes condensed.

The reader should satisfy himself that he is able in all cases to supply the reasoning in full.)

Hydrogen Chloride.—(*a*) When 1 volume of hydrogen and 1 volume of chlorine are mixed together, and the mixture exposed to diffused sunlight, hydrogen chloride is produced, the volume of the hydrogen chloride being equal to the combined volumes of hydrogen and chlorine. That is,

1 volume of hydrogen + 1 volume of chlorine give 2 volumes of hydrogen chloride.

Hence, by Avogadro's hypothesis,

1 molecule of hydrogen + 1 molecule of chlorine give 2 molecules of hydrogen chloride.

But the molecules of hydrogen and chlorine are known to be diatomic (pp. 123–125).

Hence the molecule of hydrogen chloride contains 1 atom of hydrogen and 1 atom of chlorine.

A suitable apparatus for the above experiment consists of two tubes of equal volume, connected by a tap. One of the tubes leads also through a tap to a U-tube containing mercury. (For convenience in filling the two tubes, the connecting tap may be 3-way.) After the gases have combined, the level of the mercury in the U-tube will be found to be sensibly unchanged. On disconnecting the U-tube, and connecting the remainder of the apparatus with water contained in a suitable vessel, the water will fill the whole apparatus, showing that no hydrogen or chlorine remains uncombined.

(*b*) Hydrochloric acid is monobasic.

(*c*) On placing a measured volume of hydrogen chloride over mercury in a eudiometer, and introducing a piece of sodium amalgam, the mercury will rise until the remaining gas, which will be found to be hydrogen, occupies half the volume of the original hydrogen chloride.

Both (*b*) and (*c*) lead to the conclusion that the molecule of hydrogen chloride contains only 1 atom of hydrogen.

(*d*) The molecular weight of hydrogen chloride (from its vapour density) is 36·5. But the atomic weights of hydrogen and chlorine are 1 and 35·5 respectively (see Chap. XI). Hence the molecule of hydrogen chloride contains 1 atom of each element.

Hydrogen Bromide and Hydrogen Iodide.—By analogy, we should expect the formulæ of these gases to be similar to that of hydrogen chloride. This conclusion is confirmed by applying methods (*b*), (*c*) and (*d*) to these gases.

Hydrogen Fluoride.—Silver fluoride, heated to 100° C. in contact with 1 volume of hydrogen, gives 2 volumes of hydrogen fluoride. Hence 1 molecule of hydrogen fluoride contains half a molecule (*i.e.* 1 atom) of hydrogen.

By analogy, we might expect the formula of the gas to be HF. The atomic weight of fluorine being known, by Cannizzaro's vapour density method, to be 19, the vapour density of the gas should therefore be 10. At 30·5° C., however, the V.D. has been found to be 19·66 (Mallet, 1881), which corresponds to H_2F_2. Later observers found that the V.D. varies with temperature, corresponding to formulæ ranging continuously from HF to H_3F_3. The acid itself is apparently dibasic, forming well-marked salts such as KHF_2.

Steam.—(*a*) *Empirical Formula of Water.*—A convenient apparatus consists of a eudiometer having a tap (A) at the top of the closed limb containing the spark gap, and a second tap (B) at the base of the U.

The eudiometer is completely filled with mercury, the tap A closed, and tap B opened so as to allow some mercury to run out from the closed limb. Tap A is connected with a source of oxygen, a few c.c. of the gas admitted, the mercury levelled in the two limbs, and the volume read. More than twice this volume of hydrogen is then admitted by the same means, and the volume of the mixed gases read.

The open limb is then filled with mercury, the thumb placed firmly over the end, and the mixture exploded by passing an electric spark through it. Water is formed, and condenses, occupying negligible volume. The remaining gas, which will be found to be hydrogen, is allowed to cool, the mercury levelled, and the volume of gas read.

The volume of hydrogen initially present = the volume of mixed gases minus the volume of oxygen. By subtracting from this the volume of hydrogen left at the end, we obtain the volume of hydrogen which has combined with the oxygen (see p. 281, Ex. 8).

It will be found that the oxygen has combined with twice its own volume of hydrogen; whence, since both gases are diatomic, the *empirical* formula of water is H_2O.

(*b*) *Molecular Formula of Steam*.—Hydrogen and oxygen, mixed in the proportions of 2 : 1 by volume, are introduced over mercury into a eudiometer, the limb containing the gases being kept at a constant temperature, above 100° C., by means of a jacket through which the vapour of a boiling liquid is passed. Amyl alcohol, which boils at about 130° C., is commonly used. The volume of the mixed gases is read.

The gases are exploded, and the resulting volume of steam is measured. Since the gases have been introduced in the correct proportions, there will be no residual oxygen or hydrogen.

It will be found that 2 volumes of hydrogen + 1 volume of oxygen (*i.e.* 3 volumes of the mixed gases) give 2 volumes of steam.

Whence the *molecular* formula of steam is H_2O.

Hydrogen Peroxide.—When hydrogen peroxide is decomposed (by heat, or by a catalyst such as colloidal platinum) it yields oxygen and water only. Hence it contains only hydrogen and oxygen.

By very careful distillation under reduced pressure, almost pure hydrogen peroxide can be prepared.

Thenard found that 1 volume of this purified hydrogen peroxide (which is, of course, liquid) gave 475 times its volume of oxygen at 14° C. and 760 mm.; this agrees with an empirical formula of HO.

(The density of pure hydrogen peroxide at 14° C., is about 1·45. Assuming an empirical formula of HO, 17 grams of the compound would give 5875 c.c. of oxygen at 14° C. and 760 mm. Hence 1·45 grms. (1 c.c.) would give 502 c.c. of oxygen.

The lower value actually obtained is attributed to partial volatilisation of hydrogen peroxide in the steam evolved during decomposition.)

From the freezing point of its aqueous solution, the molecular weight has been shown to be 34, which corresponds to the formula H_2O_2.

Owing to the instability of hydrogen peroxide, its vapour density has not been determined.

Ammonia.—(*a*) If a series of electric sparks be passed through a measured volume of ammonia gas contained in a eudiometer, the ammonia will be almost completely (about 98 per cent.) decomposed into nitrogen and hydrogen. It will be found that, after cooling, 2 volumes of ammonia give 4 volumes of the mixed gases. (The reason for doubling these figures will be apparent shortly.)

A measured excess of oxygen is now introduced, and the mixture exploded. All the hydrogen will combine with oxygen to form water; since 2 volumes of hydrogen combine with 1 volume of oxygen, 2/3 of the observed contraction will be due to the hydrogen which has combined. It will be found that

> 3 volumes of hydrogen are contained in the 4 volumes of nitrogen + hydrogen, obtained originally from 2 volumes of ammonia (see p. 281, Ex. 9).

Hence, on decomposition,

> 2 volumes of ammonia give 3 volumes of hydrogen and 1 volume of nitrogen.

The molecular formula of ammonia is therefore NH_3.

(*b*) If a strong solution of ammonia is dropped through a tap into a graduated tube filled with chlorine, and any excess of ammonia absorbed by the subsequent addition of dilute sulphuric acid, it will be found, on opening the tube under water, that the latter rises, filling 2/3 of the tube. The residual gas will be found to be nitrogen.

Hence, starting with 3 volumes of chlorine, 1 volume of nitrogen is finally left.

Chlorine combines with its own volume of hydrogen; hence the proportions of nitrogen : hydrogen in ammonia are as 1 : 3 by volume.

Hence the empirical formula of ammonia is NH_3. (This method does not give the molecular formula.)

(*c*) The V.D. of ammonia is 8·5; its molecular weight is therefore 17. Since $N = 14$ and $H = 1$, the molecular formula is NH_3.

(*d*) The gravimetric composition of ammonia may be found by passing dry ammonia over red-hot copper oxide, and collecting the water and nitrogen formed. In this way the empirical formula may be found to be NH_3; this, combined with a knowledge of the V.D., establishes NH_3 as the molecular formula.

Hydrogen Sulphide.—On passing a series of electric sparks through hydrogen sulphide, the gas is decomposed, sulphur being deposited and hydrogen liberated. It is found that

1 volume of hydrogen sulphide liberates 1 volume of hydrogen.

Hence

1 molecule of hydrogen sulphide contains 2 atoms of hydrogen.

(The same result is obtained if a given volume of hydrogen sulphide is enclosed in a eudiometer, and a spiral of metallic tin heated electrically in the gas; tin sulphide

is formed, and a volume of hydrogen equal in volume to that of the hydrogen sulphide is liberated.)

Neither of these results shows the number of sulphur atoms present in the molecule, but merely that the formula of hydrogen sulphide is H_2S_x.

The vapour density of hydrogen sulphide is 17 ; hence its molecular weight is 34. Of this, 2 parts are composed of hydrogen ; the remaining 32 must therefore be sulphur. But the atomic weight of sulphur is 32 (found by Cannizzaro's vapour density method, etc.) :

Hence $x = 1$, and the formula of hydrogen sulphide is H_2S.

Phosphine.—The molecular formula of this gas may be found by methods precisely similar to those used for hydrogen sulphide. On decomposing the gas by means of electric sparks, red phosphorus and hydrogen are formed. Two volumes of phosphine give 3 volumes of hydrogen ; hence the formula of phosphine is P_xH_3.

The vapour density of phosphine is 17 ; hence its molecular weight is 34. In the molecular weight, 31 parts must therefore consist of phosphorus. But 31 is the atomic weight of phosphorus (found as for sulphur).

Hence the molecular formula of phosphine is PH_3.

Silicomethane (or Monosilane).—On passing the gas through a red-hot tube, 1 volume of monosilane gives 2 volumes of hydrogen, depositing silicon.

The vapour density of monosilane is 16 ; the atomic weight of silicon is 28.

From these facts, the reader should easily be able to establish the molecular formula as SiH_4.

Hydrocarbons.—A method which may be used to find the molecular formulæ of gaseous hydrocarbons consists in exploding a measured volume of the hydrocarbon in a eudiometer with a measured excess of oxygen. Water (which condenses) and carbon dioxide are produced. The latter is absorbed with strong potash solution, and the contraction measured.

If the formula of the hydrocarbon is C_xH_y, 1 molecule of the hydrocarbon will give x molecules of carbon dioxide. Hence 1 volume of the hydrocarbon will give x volumes of carbon dioxide. If v c.c. of hydrocarbon were taken originally, the contraction observed on adding caustic potash will therefore be xv c.c. This gives x; y is then found from the original contraction observed on explosion, according to the equation

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 = xCO_2 + \frac{y}{2}H_2O$$

$$\text{volumes:} \quad v \quad + \left(x + \frac{y}{4}\right)v \quad = \quad xv \quad + \text{negligible.}$$

The volumes of gas on the left-hand side of the equation are

$$\left(1 + x + \frac{y}{4}\right)v,$$

and those on the right,

$$xv.$$

The contraction observed on explosion is, of course, equal to the L.H.S. — the R.H.S. of the equation. Knowing x and v, y can be found.

An example will make this clear.

Volume of hydrocarbon taken ..	=	8·5 c.c.
Volume of hydrocarbon + oxygen	=	43·5 c.c.
Volume after explosion	=	22·25 c.c.
Volume after treatment with KOH	=	5·25 c.c.

Contraction on adding potash = 17 = 8·5 × 2 c.c.

Therefore the formula of the hydrocarbon is C_2H_y. The equation for its combustion is

$$C_2H_y + \left(2 + \frac{y}{4}\right)O_2 = 2CO_2 + \frac{y}{2}H_2O$$

$$\text{volumes:} \quad v \quad + \left(2 + \frac{y}{4}\right)v \quad = \quad 2v \quad + \quad 0.$$

Contraction on explosion $= v + \frac{y}{4} v = 21{\cdot}25$ c.c.

Whence (since $v = 8{\cdot}5$ c.c.)

$$1 + \frac{y}{4} = \frac{21{\cdot}25}{8{\cdot}5} = 2{\cdot}5 = \frac{5}{2}.$$

Whence $y = 6$, and the formula is C_2H_6.

Ozone.—That ozone is an allotropic form of oxygen is shown by the facts that it can be prepared from pure dry oxygen only, and that on heating it decomposes to oxygen only.

(*a*) Soret's diffusion method has been already described (Chap. XIX).

(*b*) Soret also determined the formula of ozone by the following method :

Equal volumes of the same specimen of ozonised oxygen were confined in two graduated tubes standing over water (*not* over mercury, which attacks ozone). Into one tube was introduced some turpentine, which absorbs ozone, but not oxygen. A contraction of x c.c., the volume of the ozone present in the tube, was observed.

The other tube was heated to convert the ozone into oxygen, and allowed to cool to the original temperature. A permanent expansion of $\frac{x}{2}$ c.c. was observed.

Since equal volumes of the same specimen of ozonised oxygen were taken, the volumes of ozone present in both tubes must be the same, namely, x c.c. The volume of oxygen formed when this ozone is decomposed will evidently be equal to (the original volume of ozone) + (the observed permanent expansion) ; *i.e.* to $x + \frac{x}{2}$ c.c.

Hence x c.c. of ozone give $\frac{3x}{2}$ c.c. of oxygen ; or

2 volumes of ozone give 3 volumes of oxygen.

Hence, by Avogadro's hypothesis,

2 molecules of ozone give 3 molecules of oxygen.

But the oxygen molecule contains 2 atoms of oxygen.

Hence the molecule of ozone must contain $\frac{3 \times 2}{2}$, or 3 atoms of oxygen.

(3) Since the above experiments were performed, pure ozone has been prepared, and its vapour density determined by Dumas' method. The molecular weight is found to be 48, which agrees with the formula O_3 $(O = 16)$.

Carbon Dioxide.—When carbon is heated in oxygen, it burns to the dioxide. The volume of dioxide formed is equal to the volume of oxygen taken.

Hence 1 molecule of carbon dioxide must contain 1 molecule, or 2 atoms, of oxygen, and its formula must be C_xO_2.

The vapour density of carbon dioxide is 22, which gives a molecular weight of 44. Of this, 32 parts are composed of oxygen, and the remaining 12 must therefore be carbon. But 12 is the atomic weight of carbon (see Chap. XIV). Hence $x = 1$, and the formula is CO_2.

A suitable apparatus for the above experiment consists of a glass bulb fused on to a U-tube. The bulb contains a small platinum spoon, on which is placed the carbon. Touching the carbon is a fine platinum wire, which may be heated electrically to ignite the carbon. Mercury (which must be dry) is placed in the U-tube, the bulb filled with dry oxygen, and the mercury levelled in the two limbs. When combustion is complete, the gas is allowed to cool to the original temperature, and the level of the mercury will be found to be sensibly unchanged.

(Actually, a very slight contraction may be observed, due to the greater compressibility of carbon dioxide as compared with oxygen, which leads to the result that equimolecular

quantities of the two gases do not occupy exactly the same volume under the pressure of the atmosphere (see p. 216).)

Sulphur Dioxide.—The formula of this gas may be found in precisely the same way as that of carbon dioxide. The same apparatus may be used; again, a very slight contraction may be noted on cooling to the original temperature, due here to *two* causes: (*a*) the greater compressibility of sulphur dioxide as compared with oxygen, (*b*) the formation of a small amount of sulphur trioxide. Allowing for this, the results are as follows:

On burning sulphur to sulphur dioxide, the volume of dioxide formed is equal to the volume of oxygen taken.

The molecular weight of sulphur dioxide (found from its vapour density) is 64.

The atomic weight of sulphur (Cannizzaro's method, etc.) is 32.

From this it may be deduced that the molecular formula of sulphur dioxide is SO_2.

Carbon Monoxide.—If a measured volume of carbon monoxide be introduced into a eudiometer, a measured excess of oxygen added, the mixture exploded, and the carbon dioxide formed absorbed with caustic potash solution, it will be found that

> 2 volumes of carbon monoxide + 1 volume of oxygen give 2 volumes of carbon dioxide.

Knowing the molecular formulæ of carbon dioxide and oxygen to be CO_2 and O_2 respectively, it follows that that of carbon monoxide is CO.

This is supported by the fact that the vapour density of the gas is 14, which gives a molecular weight of 28 (12 + 16).

Sulphur Trioxide.—If sulphur trioxide vapour be passed through a red-hot tube, it decomposes:

> 2 volumes of vapour give 2 volumes of sulphur dioxide and 1 volume of oxygen.

Knowing the molecular formulæ of sulphur dioxide and oxygen to be SO_2 and O_2 respectively, it follows that that of sulphur trioxide is SO_3.

This is supported by the value obtained for the vapour density, and for the depression of the freezing point of a solution in phosphorus oxychloride, both of which lead to a molecular weight of 80.

Nitrous Oxide.—(*a*) If a spiral of steel wire is placed in a measured volume of the gas and heated to redness by an electric current, the iron combines with the oxygen, a volume of nitrogen being left equal, after cooling, to that of the nitrous oxide. The formula of the gas is therefore N_2O_x.

(*b*) The vapour density of nitrous oxide leads to a molecular weight of 44. Of this, 28 parts are nitrogen; therefore 16 parts are oxygen. Since the atomic weight of oxygen is 16, $x = 1$, and the formula is N_2O.

(*c*) On explosion with electrolytic gas (hydrogen and oxygen, in the proportions 2 : 1 by volume), nitrous oxide is completely decomposed into its elements; at the same time, all the electrolytic gas combines to form water. On treating the product with alkaline pyrogallol, oxygen is absorbed, and nitrogen left. It will be found that

> 2 volumes of nitrous oxide give 2 volumes of nitrogen + 1 volume of oxygen.

Hence the molecular formula is N_2O.

Nitric Oxide.—(*a*) If a spiral of iron wire is placed in a measured volume of the gas and heated to redness in an electric current, the iron combines with the oxygen, a volume of nitrogen being left equal, after cooling, to half the volume of the nitric oxide. The formula of the gas is therefore NO_x.

(*b*) The vapour density of the gas leads to a molecular weight of 30. Of this, 14 parts are nitrogen; therefore

16 parts are oxygen. Since the atomic weight of oxygen is 16, $x = 1$, and the formula is NO.

Nitrogen Peroxide.—(*a*) As with nitric oxide, a spiral of iron wire, heated in the gas, produces a volume of nitrogen equal to half the volume of the original gas, *provided that* the nitrogen peroxide be measured at a temperature somewhat above 140° C. Hence the formula of the gas at this temperature is NO_x.

(*b*) The vapour density of the gas, at 140° C., and over a certain range of temperature above this, corresponds to a molecular weight of 46, which leads to the molecular formula NO_2. At lower temperatures, the vapour density increases, approaching the value of 46, which corresponds to a molecular formula of N_2O_4. At 26·7° C. (about 5 degrees above the boiling point of liquid nitrogen peroxide) it has been calculated that the gas contains 20·1 per cent. by weight of NO_2, the rest consisting of the double molecules N_2O_4.

It is well known that the varying molecular states of the gas are accompanied by well-marked colour changes.

Nitrous and Nitric Acids.—A considerable amount of evidence might be collected regarding the molecular formulæ of these acids; the following must serve as a sample:

(*a*) The acids are both monobasic; hence they probably contain only 1 atom of hydrogen in the molecule.

(*b*) They may both be produced by the action of oxides of nitrogen upon water; hence the molecules must contain hydrogen, nitrogen, and oxygen only.

(*c*) The vapour densities of ethyl nitrite and nitrate are 37·5 and 45·5 respectively; allowing for the formula weight of the ethyl radicle, this leads to molecular weights of 47 and 63 respectively for the two acids, which correspond to HNO_2 and HNO_3.

(*d*) Potassium nitrite is oxidised by acidified potassium permanganate to nitrate; the equivalent weight of

potassium nitrite in this reaction is 42·5, which corresponds to the reaction

$$KNO_2 + O = KNO_3.$$

Other confirmatory evidence will probably occur to the reader: *e.g.* the behaviour of ammonium nitrite and nitrate on heating, the percentage compositions, as well as the vapour densities, of other organic esters of the acids, and so forth.

Nitrous Anhydride.—On cooling the vapours obtained by distilling moderately dilute nitric acid with arsenious oxide, a dark blue liquid is obtained. The vapour of this is completely absorbed by caustic soda, forming sodium nitrite. Presumably, therefore, this substance is nitrous anhydride, of empirical formula N_2O_3.

The vapour density, however, indicates that the gas is decomposed into equal volumes of nitric oxide and nitrogen peroxide, unless the liquid is specially dried by long exposure to phosphorus pentoxide, when it appears to yield a vapour largely of composition N_4O_6.

Nitric Anhydride.—This may be prepared by dehydrating concentrated nitric acid with phosphorus pentoxide; it is therefore presumably the anhydride of nitric acid, N_2O_5. Below 29·5° C. it is a solid; on melting it gives a liquid which decomposes into nitrogen peroxide and oxygen; it dissolves in water to form nitric acid.

All the evidence thus points to the formula N_2O_5 for this compound.

Nitrosyl Chloride.—This is a gaseous compound, absorbed by water, forming nitrous and hydrochloric acids. The proportions in which these acids are present may be estimated by titration with cold dilute permanganate and silver nitrate solutions respectively. It will be found that 2 equivalents of nitrous acid are formed

for 1 equivalent of hydrochloric. This agrees with the empirical formula NOCl:

$$NOCl + H_2O = HNO_2 + HCl.$$

This is supported by the value obtained for the vapour density of the gas.

Sulphuryl Chloride.—This substance, which is a liquid boiling at 69°, is formed by the direct combination of sulphur dioxide and chlorine. It has, therefore, the formula $S_xO_{2x}Cl_y$.

The molecular weight, found from the vapour density, is 135; giving x the value of 1, 64 parts of the molecular weight would be due to sulphur and oxygen, leaving 71 for chlorine.

The formula is therefore probably SO_2Cl_2. This is supported by a number of facts; *e.g.*:

(*a*) When completely hydrolysed by water, 1 molecule of sulphuric acid and 2 molecules of hydrochloric are formed. (This may also be taken as indicating the formula of the dibasic sulphuric acid, if that of sulphuryl chloride is regarded as sufficiently proved.)

(*b*) Hydrolysis may take place in two stages, the intermediate compound having the constitution $SO_2(OH)Cl$.

The above examples should illustrate sufficiently the ways in which evidence may be interpreted in order to establish molecular formulæ; many other examples, involving the general method of determining percentage compositions and molecular weights, have been given in other chapters.

Exercises on Chapter XX

1. Find the molecular formula of a gaseous hydrocarbon from the following data:

Volume of hydrocarbon	=	15·6 c.c.
Volume after adding oxygen	=	60·0 c.c.
Volume after explosion	=	28·8 c.c.
Volume after adding KOH soln.	=	13·2 c.c.

2. Find the molecular formula of a gaseous hydrocarbon from the following data :

Volume of hydrocarbon	=	9·4 c.c.
Volume after adding oxygen	=	63·7 c.c.
Volume after explosion	=	40·2 c.c.
Volume after adding KOH soln.	=	12·0 c.c.

3. *Compounds of Phosphorus.*

(*a*) A liquid compound, formed by the direct combination of phosphorus and chlorine, dissolves in water, forming phosphorous and hydrochloric acids.

0·126 grm. of this compound was dissolved in water, and the chlorine precipitated as silver chloride. 0·394 grm. of the latter was obtained.

Calculate the empirical formula of the compound. (P = 31, Cl = 35·5, Ag = 108.)

Given that its vapour density lies between 68 and 69, find its molecular formula, and suggest a probable formula for phosphorous acid. What further evidence would be desirable in order to confirm the latter ?

(*b*) The above chloride of phosphorus, mixed with powdered potassium chlorate, and distilled, yields a compound, X, of vapour density approximately 77. On treatment with water, X yields hydrochloric acid and a tribasic oxyacid of phosphorus. By this means it may readily be shown that the compound X contains 69·4 per cent. of chlorine.

Find the probable molecular formulæ (*a*) of X, (*b*) of the oxyacid of phosphorus formed when X reacts with water.

The same oxyacid of phosphorus can also be formed by the action upon boiling water of an oxide of phosphorus containing 56·3 per cent. of oxygen. Show that this confirms the formula suggested for the acid. (O = 16.)

4. When a mixture of equal volumes of carbon monoxide and chlorine is passed over heated charcoal, a gaseous compound, A, is produced which is readily hydrolysed by water to carbonic acid and hydrochloric acid.

The gas A contains 71·7 per cent. of chlorine, and has a vapour density of 49–50.

Find the molecular formula of A. (C = 12, O = 16, Cl = 35·5.)

5. A deep red liquid dissolves in water, forming a mixture of chromic acid and hydrochloric acid.

0·149 grm. of the liquid, so treated, was found to oxidise 28·8 c.c. of $N/10$ ferrous sulphate solution; and on precipitating the chlorine ions formed at the same time as silver chloride, 0·276 grm. of chloride was obtained.

Find its empirical formula. ($Cr = 52$, $O = 16$, $Cl = 35·5$, $Ag = 108$.)

6. How would you show (*a*) that ammonia contains only nitrogen and hydrogen, (*b*) that a given gaseous hydrocarbon contains only carbon and hydrogen, (*c*) that nitrous oxide, nitric oxide, and nitrogen peroxide contain only nitrogen and oxygen?

7. Complete the reasoning, outlined in this chapter, necessary to establish the molecular formulæ of (*a*) monosilane, (*b*) carbon monoxide, (*c*) sulphur dioxide, (*d*) sulphur trioxide.

8. Calculate the empirical formula of water from the following data:

Volume of oxygen taken	= 13·6 c.c.
Volume of oxygen and hydrogen	= 60·5 c.c.
Volume of hydrogen after explosion	= 19·7 c.c.

9. Calculate the molecular formula of ammonia from the following data:

Volume of ammonia taken	= 17·3 c.c.
Volume after prolonged sparking	= 34·5 c.c.
Volume after adding oxygen	= 52·5 c.c.
Volume after explosion	= 13·6 c.c.

CHAPTER XXI

CONCEPTIONS OLD AND NEW

"A normal atom consists of a central nucleus around which a number of electrons revolve in orbital motion like planets round the sun."—SIR JAMES JEANS, *Eos* (1928).

"Quod superius est sicut quod inferius et quod inferius est sicut quod superius ad perpetranda miracula rei unius."—From the *Tabula Smaragdina*, attributed to Hermes, patron of alchemy. (Date unknown: prior to 13th cent. A.D.)

LET us, before considering the many and profound changes which have taken place of recent years in our conceptions of atoms and molecules, briefly review that part of the story which has been given in the preceding chapters.

We have seen that the Greeks were the first to speculate systematically upon the nature of matter; and that two philosophic schools arose, one attempting to account for the diversity of matter by supposing that there existed one fundamental substance, in the form of minute particles differing in size, shape, and motion; while the other conceived that all matter was built up of four elements, earth, air, fire, and water, mingled in varying proportions. The former school came nearer to our modern notions; but the latter, championed by Aristotle, held sway for nearly 2000 years, being strangely transformed in the hands of the alchemists during the Middle Ages. Whatever may have been the true aims of the alchemists—whether they sought simply to transmute base metals into gold, or whether their quest was in reality entirely mystical—it must be conceded that they contributed little of value to chemistry in its modern

sense, beyond accumulating a good many empirical observations.

Little better, from this point of view, than the alchemists were the "iatrochemists," who, though they did something to bring chemistry down to solid earth, still regarded it largely as a means to an end.

Modern science dates from that astonishing outburst of spiritual, intellectual and artistic activity known as the Renaissance. The genius of the Renaissance was essentially a youthful one. Paradoxically, though it owed its impetus largely to the rediscovery of ancient learning, it consisted to a great extent in the overthrow of tradition and the development of new ideas. Painting broke free from an influence which had become frozen and sterile; and just as the architects of Italy made use of the classical orders to produce something quite original, so many of the philosophic notions of the Greeks were absorbed by the thinkers of the Renaissance, and given a new direction.

In science, the essentially new feature lay in the application of the method of induction, combined with a gradual realisation of the necessity of quantitative measurement of observed phenomena. Chemistry lagged for some time behind mechanics, astronomy, and other branches of physics in this respect; and Boyle's *Sceptical Chymist*, though an admirable example of the critical spirit then current, was in advance of its age. Nevertheless, the years which followed saw the introduction into chemistry of quantitative measurement, by Cavendish, Black, Lavoisier, and others. Though Lavoisier is chiefly familiar to the casual student of historical chemistry as the man who overthrew the theory of phlogiston, it may be said with reason that his chief work lay in impressing upon his contemporaries the necessity of placing chemistry among the exact sciences by means of quantitative experiment. As a result of this, many of the problems posed by Boyle found a satisfactory solution; and the

end of the eighteenth century saw the establishment of the laws of Conservation of Mass, Constant Proportions, and Reciprocal Proportions, the last introducing the fundamentally important conception of the " chemical equivalent."

The first decade of the nineteenth century saw the publication of Dalton's Atomic Theory. It may be repeated here that the importance of this theory lay in the possibility of deducing from it the law of Multiple Proportions, which was verified by experiment in many instances. Here for the first time was tangible evidence of the existence of atoms. The truth of the law was undoubted ; and Dalton's theory alone could provide a simple explanation of it. Hitherto theories of the atomic constitution of matter had been hardly more than speculations ; it had been shown that a molecular theory was compatible with some of the properties of gases and liquids, but it could not have been said that such a theory was the only one which could provide a plausible explanation of these properties.

Shortly afterwards (though its importance was not realised at the time) Avogadro advanced his famous hypothesis ; and about the middle of the century Cannizzaro showed how this hypothesis could be applied to the problem of determining the relative weights of molecules and atoms. His deductions were linked up with the laws of Dulong and Petit and of isomorphism ; and the way was now clear to the establishment of empirical and molecular formulæ. By the year 1875 the Periodic Classification of the elements had won general acceptance. Its position was further strengthened by later discovery of the rare gases of the atmosphere.

The twentieth century has seen many modifications in our conception of atoms and molecules. It had been shown in 1897, by Sir J. J. Thomson, that there existed particles of matter much smaller than any known atom. These particles were found to be associated with a definite

charge of negative electricity, and the name " electrons " has been given to them. About the same time it was established that certain minerals emitted radiation of three types : (*a*) a stream of negatively charged particles, known as β-particles, and identified with electrons ; (*b*) a stream of positively charged particles, or α-particles, found to be identical with helium atoms which had lost two electrons each ; and (*c*) a γ-radiation of the same nature as light, though of much shorter wave-length.

This " radioactivity," as it was called, was found to be due to the presence in the minerals of certain metals, among which were radium, uranium, and thorium, the atoms of which were actually in a process of disintegration. They passed through a series of changes, too complex to describe here, and appeared to break down finally into lead. A remarkable consequence of this was that atoms of lead, derived from one radioactive element, should have weights different from those derived from another radioactive element. Lead derived from uranium or radium should have an atomic weight of 206, while that from thorium should have an atomic weight of 208.

This deduction was put to the test, and it was found that lead obtained from minerals containing uranium and radium, but little or no thorium, might have an atomic weight as low as 206·5, while that from thorium minerals gave values as high as 207·9. (The accepted value for the atomic weight of ordinary lead is 207·2.)

As the result of these discoveries, it was realised that the atom was a more complex structure than had previously been supposed. The theory of the atom, developed by Rutherford and others, was that the atom consists of a number of electrons revolving round a positively charged nucleus. Since the atom in its normal state (*i.e.* except when " ionised ") is electrically neutral, the positive charge on the nucleus must be exactly equal to the combined negative charges on the electrons. If an

atom possesses n of these outer electrons, each of charge $-e$, the charge on the nucleus must be $+ne$. n is known as the "atomic number." Upon the number and arrangement of these electrons appear to depend most of the chemical and physical properties of the element.

Further investigation, largely by Moseley, a brilliant young English physicist who was killed during the War, led to the identification of the atomic number with the number of the element in the Periodic Table, starting with hydrogen as unity, and proceeding onwards (He = 2, Li = 3, etc.). It was found that in order to assign correct atomic numbers to all the elements, the strict order of atomic weights had in a few cases to be reversed; *and that these were just those cases in which the order of the atomic weights had been found to be anomalous* (*cf.* Chaps. XIII, XV). Thus the atomic numbers of iron, cobalt and nickel were found to be 26, 27 and 28, which places the elements in the natural order with respect to their general physical and chemical properties, whereas the order of increasing atomic weight would give Fe (55·84), Ni (58·68), Co (58·97).

It was thus definitely shown that the atomic number of the atom was of an importance more fundamental than the atomic weight. Immediately after the War, F. W. Aston, improving upon an earlier apparatus of Sir J. J. Thomson's, was able to demonstrate that other elements might consist of atoms of unequal masses. The apparatus he used, now known as the "mass spectroscope," depends upon the following principle:

When gases or vapours are exposed, at a high vacuum, to an electric discharge, some of the atoms lose one or more electrons, becoming in consequence positively ionised. They will then travel at high speed towards the negative pole in the vacuum tube. During their passage they are exposed to a combined electric and magnetic field. They suffer a deflection; and by allowing them to fall subsequently upon a photographic plate, the magnitude of this

deflection can be calculated. From this it is possible to work out the ratio $\frac{\text{charge on the atom}}{\text{mass of the atom}}$. Since the charge on the ionised atom must be $+xe$, where $-e$ is the charge on an electron, and x is a small whole number (usually 1 or 2), the masses of the individual atoms can be estimated.

In this way, Aston was early able to show that the element neon (atomic weight 20·2) consisted of two kinds of atoms, of mass 20 and 22 ($O = 16$). Chlorine, of atomic weight 35·46, consisted mainly of two kinds of atoms, of mass 35 and 37. From the intensities of the lines on the photographic plate, it was possible to estimate the relative proportions in which the atoms of different kinds occurred; and it was shown to agree with the conclusion that the "atomic weights" determined by chemical analysis were in reality mean values, dependent upon the masses of the different "isotopes," as they are called, and upon the proportions in which these isotopes are present. With chlorine, for example, the isotope of mass 35 occurs in greater proportion; hence the mean atomic weight of chlorine lies nearer to 35 than to 37.

A long-standing mystery, that of the "anomalies of the Periodic Table," was thus cleared up. It will be remembered that the atomic weight of argon (39·88) was found to be greater than that of potassium (39·10); whereas there was no doubt that argon should come before potassium in the Periodic Classification.* It has been found that argon consists of at least two isotopes, of masses 40 and 36, the former occurring in the greater proportion, while potassium consists of two isotopes of masses 39 and 41, the former in the greater proportion. The net result is that the mean atomic weight of argon is greater than that of potassium. The remaining anomalies are

* Cf. Chap. XV.

similarly explained, as will be seen from the following table :

	Atomic Weight.	Masses of Isotopes, in order of Intensity.
Iron	55·84	56, 54
Cobalt..	58·97	59
Nickel	58·68	58, 60
Tellurium	127·5	128, 130, 126
Iodine	126·92	127

Space will not permit of a full list of all the isotopes the existence of which has been established. One or two examples of special interest may be mentioned.

Hydrogen.—Atoms apparently all of one kind, of mass 1·0078 (O = 16).

Oxygen consists almost entirely of one isotope, of mass 16·000 (by definition). Recently, however (1929), the existence of heavier isotopes, of mass 17 and 18, has been established. It is possible that this may lead to a readjustment of the standard of atomic weights, though these isotopes occur in such small quantity that even the most accurate chemical analyses can hardly be affected.*

Tin.—Eleven isotopes, of masses ranging from 112 to 124.

It was at first thought that, though the atomic weights of the elements were obviously not whole numbers (taking O = 16), those of the isotopes might be. This has not proved to be the case. It was shown almost at once that the atomic weight of hydrogen (1·008) was not due to the existence of a heavier isotope of hydrogen, but was a true indication of the relative weight of the atom. With improved apparatus, Aston has been able

* If the mass of the main isotope of oxygen is made exactly 16, the mean atomic weight of oxygen will differ slightly from this.

to show that real deviations from whole numbers occur with nearly all elements, though the deviations are in general much slighter. Thus, taking the oxygen isotope of mass 16 as the standard (16·0000), the two main isotopes of neon have masses 20·0004 and 22·0048; the atom of phosphorus a mass 30·9825, etc.

It is now thought possible that all elements may have isotopes, though any undiscovered up to the year 1928 must be present in very small quantity.

The discovery of isotopes, and in particular the variation observed in the atomic weight of lead from different sources, naturally led to the query as to whether all atomic weights were variable. Fortunately for the validity of gravimetric analyses, the answer appears to be in the negative. The atomic weight of chlorine has been determined with great care, using specimens of chlorine from the most varied sources, and no sensible deviation from the mean value previously established has been found. Other analyses have yielded equally negative results; it was thought recently that a variation in the atomic weight of boron had been established, but it appears that the results are not conclusive. It seems, then, that the proportions of the isotopes of all the non-radioactive elements (except lead) are naturally fixed, and that the table of atomic weights is unlikely to suffer any revolutionary changes.

We must, however, admit a technical alteration in some of the stoichiometric laws of chemical combination. Evidently the combination of sodium (atoms of mass 23) with chlorine can result in two forms of sodium chloride, in which the proportions of sodium to chlorine are as 23 : 35 and 23 : 37. The law of Constant Proportions may therefore be modified to the statement:

"*The same compound always contains the same elements united in the same proportions by atoms.*"

Owing to the constant distribution of isotopes, the

modification does not, however, affect the ordinarv operations of analysis.

The preceding observations may be summarised as follows :

A given atom consists of a small positively charged nucleus, surrounded with electrons. Most of the mass of the atom is situated in the nucleus.

The fundamental property of the atom, which determines the number of electrons external to the nucleus, is the "atomic number." If the charge on an electron is $-e$, and the atom possesses n external electrons, the charge on the nucleus will be $+ne$. The atomic number, n, is thus equal to the number of external electrons in the atom.

All the atoms of a given element have the same atomic number ; their masses may, however, be different from one another. Atoms of a given element, of the same atomic number but different masses, are known as isotopes.

The atomic weight of an element, as found by ordinary means, is determined by the masses of its isotopes, and by the proportions in which they occur. These proportions seem to be fixed, with the exceptions of the radioactive elements and lead.

The Periodic Law may be re-stated in the form :

" *The physical and chemical properties of the elements are periodic functions of their atomic numbers.*"

The Molecule, and Theories of Valency.—In the preceding chapters of this book we have adhered to the definition of " molecule " which resulted from the theories of Avogadro, namely, that the molecule is " the smallest particle of an element or compound which can normally lead a separate existence." This definition is adequate for many purposes. When the element or compound exists as a gas, there is no doubt that individual molecules are present in it, moving about as a whole. The same

is true of those substances in solution which give "normal" values of osmotic pressure, depression of the freezing point, etc.

The simple conception of "valency," as the ratio of atomic weight to equivalent weight, proved of immense value in systematising chemical knowledge.

In organic chemistry, in particular, the molecular formula of a given compound having been established by the methods considered above, it is usually possible to assign to it a "constitutional formula," by giving carbon a valency of 4 and oxygen a valency of 2 (that of hydrogen being equal to 1). In many instances two or more structural formulæ are possible for a compound of given molecular formula; and it has been found that such compounds actually exist, possessing the same molecular formula, but different properties.

Valency has sometimes been called the "combining power," or "saturation capacity," of the atom. Thus we may say that the atom of carbon is "saturated," when it combines with 4 atoms of hydrogen, 4 of chlorine, or 2 of oxygen. But such a simple idea does not really cover the facts. To take an example: magnesium has a valency of 2, combining with chlorine to form the chloride $MgCl_2$. But this compound can further combine with water, forming the hydrate $MgCl_2,6H_2O$; and this hydrate can form a double salt with potassium chloride, $KCl,MgCl_2,6H_2O$. What is the valency of magnesium in these compounds?

Again, many cases are known in which compounds can associate into double or triple molecules; acetic acid, for example, when dissolved in benzene, consists largely of the molecules $(C_2H_4O_2)_2$.

Such facts indicate that even when the atom combines with other atoms to form molecules, thereby exerting its normal valency, there may still exist a "residual field of force" around the molecule, which enables it to combine further with other molecules. The very existence

of solids and liquids, of course, indicates the existence of attractive forces between molecules; and van der Waals' equation takes account of the persistence of this attractive force even in gases.

Many theories of valency were elaborated during the past few decades, distinguishing between "normal" and "residual" valencies, and so forth. It is now known that the atom is electrical in structure; and though we are still largely ignorant of the forces within it, we have some general idea of its constitution. Theories of valency are hence concerned, at the present time, with establishing the connection, which must exist, between the structure of the atom and the ways in which it may combine with other atoms; and also with the still more difficult task of estimating the nature of the resulting field of force around the molecule.

Assistance, increasing yearly in value, is forthcoming from the recent application of X-rays to the elucidation of the arrangement of atoms in solid substances. Usually, when a substance is known to exist only in the solid state, the empirical formula only is written for it, since there may be no means of determining its molecular weight. We are now able, however, to determine in many cases the actual arrangement of the atoms in the solid; and though we are still far from understanding all the forces which determine the arrangement, knowledge of the latter is obviously of the greatest help in approaching the problem.

It would take far too long to explain the method in detail; we may, however, take one example, that of sodium chloride, to illustrate in outline the kind of progress that has been made. Sodium chloride has the empirical formula NaCl; the old type of "structural formula" of this compound would be Na — Cl, which tells us only that 1 atom of sodium is presumed to be united to 1 of chlorine, forming a molecule of sodium chloride.

Sodium chloride exists in crystals of cubic shape.

X-ray analysis shows that in a crystal of sodium chloride the atoms of sodium and chlorine occur alternately, being built up in a cubic structure (Fig. 12). One atom of sodium is symmetrically surrounded by six chlorine atoms, and one atom of chlorine by six sodium atoms. There is no indication that one atom of chlorine is specially attached to any one atom of sodium.

When it dissolves in water, sodium chloride is known to split up into ions, the sodium atom carrying a positive charge (*i.e.* having lost an electron) and the chlorine a negative charge (having gained an electron). The modern view is that these ions exist also in the solid salt; and that the crystal is really a regular assemblage of ions of sodium and of chlorine.

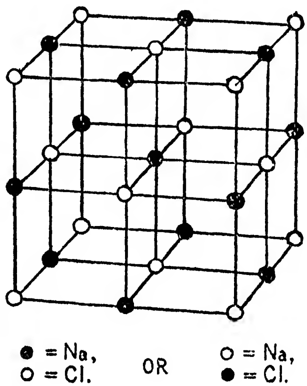

FIG 12.

Hence the term " molecular formula " has no meaning in the case of sodium chloride, and the empirical formula " serves every useful purpose." (Caven, see reference at end of chapter.)

It may be asked whether similar conclusions hold good for all solid substances. The answer is that all crystals consist of a regular arrangement of atoms, though in some cases the arrangement may be very complex compared with that of sodium chloride. But, in organic compounds especially, the molecule may continue to exist within the " lattice " structure of the crystal ; and when the compound is vaporised or dissolved, these molecules break apart and then lead a separate existence. With inorganic salts, on the contrary, the structure seems to be usually ionic, as with common salt.

It has been known for some time (ever since the experiments of Raoult, and their explanation by Arrhenius) that inorganic salts ionise in aqueous solution ; and the newer theories of valency postulate a distinction between combination such as that between sodium and chlorine, which involves ionisation, and that between carbon and hydrogen, which does not involve ionisation. Both are, however, electrical in nature.

General Conclusion.—The trend of recent years may be described as the attempt to explore the structure of individual molecules and atoms, and to elucidate the forces which govern their behaviour. Owing to the refinements of modern technique, it is now possible to deal with small numbers of atoms and molecules, whereas previously even the most delicate analyses dealt with thousands of millions of them. The results obtained so far have modified profoundly our conceptions of mass, energy, and other fundamental quantities.

Though the atom has been likened to the solar system, it would be a mistake to imagine that the analogy is in reality exact. Newtonian mechanics (at least as modified by the theory of relativity) has proved on the whole competent to deal with the solar system ; but it became apparent quite early that the atom behaved in a way which seemed quite inexplicable on the basis of classical electromagnetic theory (*i.e.* the theory which has resulted from the application of Newtonian mechanics to electricity and magnetism). It is as yet too early to say how far the classical theory may have to be modified ; perhaps it may have to be remodelled altogether. On the other hand, our present difficulties may be at least partly resolved when the nature of the electron is more fully understood.

The author has tried, throughout this book, to make clear the general lines upon which one branch of theoretical chemistry has developed ; to show how by the

inductive method knowledge may be gradually extended; how facts apparently unrelated have been found to be connected; and how mysterious exceptions to general rules may be explained in the light of further discoveries. Though certain theories (such as that of phlogiston) may have to be abandoned, it is not true to state sweepingly that all scientific theories share such a fate. Even a theory which proves eventually untenable may have produced useful results during its life; the phlogiston theory, for example, served to connect a number of phenomena, such as oxidation and reduction, together; and when the later, oxygen, theory was established, it was seen that the connection between the phenomena was a real one, though previously imperfectly explained.

More often, perhaps, a theory is not abandoned, but gradually modified and elaborated. This is conspicuously the case with the atomic theory; we have ceased now to argue whether atoms exist; the evidence for their existence is now overwhelming. But the atom is a much more complex affair than Dalton imagined; and the original simple postulates of his theory have proved inadequate.

So is it likely to be; and he would be a rash man who maintained that any of our present scientific theories were unlikely to be modified any further. Science is always progressing, and our views are always changing. But the methods which lead to progress remain the same, and he who has trained his mind by the study of the pioneer work of the nineteenth century, in the spirit described by Faraday in the passage quoted at the beginning of this book, should be well equipped to deal with the problems with which we are contending, on an extended frontier, in the twentieth.

References to Chapter XXI

From a vast literature dealing with modern aspects of the atomic and molecular theories, the following books may be selected:

Atoms and Molecules, by R. M. Caven (see ref. to Chap. XIII).

Isotopes, by F. W. Aston.

X-rays and Crystal Structure, by Sir William and W. L. Bragg.

Concerning the Nature of Things, by Sir William Bragg (G. Bell & Sons, 6*s*.). A most delightful account of modern molecular theory, requiring little or no specialised knowledge from the reader.

Cambridge Readings, by W. C. Dampier-Whetham (see ref. to Chap. X).

Valuable summaries of recent papers will be found in the Annual Reports of the Chemical Society. Every two years (1926, 1928 . . .) a special section is given dealing with Sub-atomic Phenomena and Radioactivity.

HISTORICAL TABLE

(In this Table, a number of outstanding events and personalities in the history of chemistry will be found on the left, and in that of other sciences on the right.)

GREEK SCIENCE AND PHILOSOPHY
circ. 500–200 B.C.

Lucretius, 98–55 B.C.

(*School of Alexandria*—early astronomy, medicine, etc.—*fl. circ.* 3rd cent. B.C. for some hundreds of years. Galen, teacher of medicine, *fl. circ.* 150–200 A.D.)

ALCHEMICAL PERIOD (3rd cent. A.D. onwards). Coincides with "Dark Ages" in Europe, *circ.* 300–1100 A.D.	ARABIAN SCIENCE AND ALCHEMY flourished from *circ.* 600–1100 A.D.

RENAISSANCE IN EUROPE

Revival of learning, largely through classical culture reaching Europe *viâ* Arabia.

"IATROCHEMISTRY," *circ.* 1550–1700 A.D. (Paracelsus, van Helmont, etc.)	Leonardo da Vinci, 1452–1519.
	Francis Bacon, 1561–1626.
	ASTRONOMY AND MECHANICS.
	Copernicus (heliocentric theory), 1473–1543.
Robert Boyle, 1626–1691.	Galileo, 1564–1642.
	Newton, 1642–1727.
	BIOLOGY.
	Circulation of the blood (Harvey, 1578–1657).

PHILOGISTON THEORY, *circ.* 1670–1770. Cavendish, 1731–1810. Priestley, 1733–1804.	
OXYGEN THEORY. Lavoisier, 1743–1794.	
LAWS OF CONSERVATION OF MASS, etc., established *circ.* 1800.	
ATOMIC THEORY OF DALTON, 1804–1808.	FARADAY'S RESEARCHES IN ELECTRICITY, *circ.* 1830 onwards.
GAY-LUSSAC'S LAW, 1810.	"WAVE THEORY OF LIGHT," *circ.* 1800–1830.
AVOGADRO'S HYPOTHESIS, 1811.	
	MECHANICAL EQUIVALENT OF HEAT, *circ.* 1840–1850.
CANNIZZARO'S PAPER, 1858.	ORIGIN OF SPECIES PUBLISHED, 1859.
PERIODIC LAW, 1870.	
ARRHENIUS' THEORY OF ELECTROLYTIC DISSOCIATION, 1887.	
DISCOVERY OF RARE GASES, GASES, 1895–1898.	
MEASUREMENT OF *e/m* FOR ELECTRON, 1897.	
SEPARATION OF RADIUM, 1900.	MENDELIAN THEORY REDISCOVERED, 1900.

Era of "ATOMIC PHYSICS," 1900 onwards. (QUANTUM THEORY, 1901 ; BOHR THEORY OF ATOM, 1913 ; QUANTUM AND WAVE MECHANICS, 1925–1926.)

	SPECIAL THEORY OF RELATIVITY, 1905.

ANSWERS TO SOME NUMERICAL PROBLEMS

Chapter VIII

No. 6. The two equivalent weights of the metal are in the ratio of 2 : 1.

Chapter XIV

(*a*) 134·7, taking O = 16. Berzelius took O = 8, when At. Wt. becomes 67·4.

(*b*) 51·36 (O = 16).

Chapter XV

No. 5. At. Wt. = 39·9.

Chapter XVI

No. 1. 119
No. 2. At. Wt. Cr = 52.
No. 3. At. Wt. Fe = 55·8.
No. 4. At. Wt. Cu = 63·6.
No. 5. At. Wt. Se = 79.
No. 6. At. Wt. Ga = 70·1.
No. 7. At. Wt. Rb = 85·4.
No. 8. At. Wt. Zn = 65·4.
No. 9. At. Wt. Ag = 108

Chapter XVII

No. 1. 260.
No. 2. 58·2.
No. 3. 60.
No. 4. $C_3H_6O_2$.
No. 5. CH_4O.
No. 6. $C_4H_8O_2$.
No. 7. 2 atoms.

Chapter XVIII

No. 1. 144.
No. 2. 102.
No. 3. Mean value 128·1.
No. 4. 162.
No. 5. 18·9.
No. 6. $C_6H_{12}O_6$.
No. 7. $C_{14}H_x$; x probably = 10.
No. 8. 1·31, 1·30, 0·69 atmos.; 9·5 per cent.
No. 9. 342.
No. 10. $C_6H_{12}O_6$.

Chapter XX

No. 1. CH_4
No. 2. C_3H_6.

INDEX

THE END

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